TESE DE DOUTORAMENTO

DESIGN AND DEVELOPMENT OF NANOLUBRICANTS FOR THE PRODUCTION AND EFFICIENT USE OF THE ENERGY

José Manuel Liñeira del Río

ESCOLA DE DOUTORAMENTO INTERNACIONAL

PROGRAMA DE DOUTORAMENTO EN ENXEÑARÍA TERMODINÁMICA DE FLUÍDOS

SANTIAGO DE COMPOSTELA

2020

USC
UNIVERSIDADE
DE SANTIAGO
DE COMPOSTELA

DECLARACIÓN DO AUTOR/A DA TESE

Design and development of nanolubricants for the production and efficient use of the energy

D. José Manuel Liñeira del Río

Presento a miña tese, seguindo o procedemento axeitado ao Regulamento, e declaro que:

1) A tese abarca os resultados da elaboración do meu traballo.
2) De selo caso, na tese faise referencia ás colaboracións que tivo este traballo.
3) A tese é a versión definitiva presentada para a súa defensa e coincide coa versión enviada en formato electrónico.
4) Confirmo que a tese non incorre en ningún tipo de plaxio doutros autores nin de traballos presentados por min para a obtención doutros títulos.

En Santiago de Compostela, 28 de abril de 2020

Asdo. José Manuel Liñeira del Río

USC
UNIVERSIDADE
DE SANTIAGO
DE COMPOSTELA

AUTORIZACIÓN DO DIRECTOR / TITOR DA TESE

Design and development of nanolubricants for the production and efficient use of the energy

Dna. Josefa Fernández Pérez
e
Dna. Enriqueta López Iglesias

INFORMAN:

Que a presente tese, correspóndese co traballo realizado por D. José Manuel Liñeira del Río, baixo a nosa dirección, e autorizamos a súa presentación, considerando que reúne os requisitos esixidos no Regulamento de Estudos de Doutoramento da USC, e que como directoras desta non incorremos nas causas de abstención establecidas na Lei 40/2015.

De acordo co artigo 41 do Regulamento de Estudos de Doutoramento, declaramos tamén que a presente tese de doutoramento é idónea para ser defendida en base á modalidade de COMPENDIO DE PUBLICACIÓNS, nos que a participación do doutorando foi decisiva para a súa elaboración.

A utilización destes artigos nesta memoria, está en coñecemento dos coautores, tanto doutores como non doutores. Ademais, estes últimos teñen coñecemento de que ningún dos traballos aquí reunidos poderá ser presentado en ningunha outra tese de doutoramento.

En Santiago de Compostela, 28 de abril de 2020

Asdo. Dna. Josefa Fernández Pérez　　　　Dna. Enriqueta López Iglesias

USC
UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

ABSTRACT

Technological advances in lubrication are essential to improve the mobility, durability, efficiency of machinery as well as to reduce carbon dioxide emissions. On the other hand, it is considered that nanotechnology will play a leading role in the technological advances of the 21st century. Several publications have already shown that nanoadditives can reduce friction and/or wear in mechanical systems. Thus, combining both fields, the main objective of this Doctoral Thesis is to design and characterize nanolubricants formed by the addition of nanomaterials in different base oils. Specifically, this Doctoral Thesis focuses on the tribological and thermophysical study of lubricants formed by base oils (esters and polyalphaolefins) and different nanomaterials as additives. For this purpose, graphene nanoplatelets, reduced graphene oxide nanosheets, hexagonal boron nitride nanoparticles, magnetite of different sizes (6.3 and 10 nm) nanoparticles as well as a neodymium alloy nanoparticles were used. Both base oils and nanoadditives were characterized by numerous techniques.

A deep stability analysis was carried out for all the studied nanolubricants by different methods, observing that this is the main problem to obtain potential lubricants for use in industrial applications. For this reason, the use of dispersants, including an ionic liquid, has been studied and four nanoadditives were chemically modified in order to achieve good stability of the nanolubricants. Nanolubricants with a temporal stability of up to 11 months were obtained.

To design new lubricants, it is important to examine how the addition of nanoadditives influences their thermophysical properties, since these affect the performance of the lubricant. For this purpose, density and viscosity at atmospheric pressure of base oils and designed nanolubricants were studied. The effect of the concentration of three types of nanoparticles on the values of these thermophysical properties for nanolubricants based on two base oils has been quantified.

For the technical application of nanolubricants it is critical to know their tribological behavior. This PhD Thesis has mainly focused on developing tribological tests to determine the coefficient of friction, the film thickness as well as analyzing the wear produced during these tests. Four different tribological devices were used to measure the friction whereas a 3D Optical profilometer was utilized to quantify the produced wear. Reductions in friction and wear (track width) of up to 36% and 67%, respectively, have been obtained. The wear

UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

reduction mechanisms of nanoadditives were studied by means of scanning electron microscopy and confocal Raman microscopy, among others.

Keywords: nanolubricants, base oils, nanoparticles, nanomaterials, ionic liquids, additives, friction, wear, film thickness, thermophysical properties.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

RESUMEN

Los avances tecnológicos en materia de lubricación son esenciales para mejorar la movilidad, durabilidad o la eficiencia de la maquinaria, así como para reducir las emisiones de dióxido de carbono. Por otro lado, se considera que la nanotecnología desempeñará un papel de liderazgo en los avances tecnológicos del siglo XXI. Diversas publicaciones ya han demostrado que los nanoaditivos pueden reducir la fricción y/o el desgaste en sistemas mecánicos. Así, combinando ambos campos, el objetivo principal de esta Tesis Doctoral es diseñar y caracterizar nanolubricantes formados por la adición de nanomateriales en diferentes aceites base. En particular, esta Tesis Doctoral se centra en el estudio tribológico y termofísico de lubricantes formados por aceites base (ésteres y polialfaolefinas) y diferentes nanomateriales en forma de aditivos. Para ello se emplearon nanoplaquetas de grafeno, nanoláminas de óxido de grafeno reducido y nanopartículas de nitruro de boro hexagonal, de magnetita de distintos tamaños (6.3 y 10 nm), así como de una aleación de neodimio. Tanto los aceites base como las nanoaditivos han sido caracterizados mediante numerosas técnicas.

Se ha llevado a cabo un profundo análisis de estabilidad de todos los nanolubricantes estudiados por diferentes métodos, observando que éste es el principal problema para conseguir potenciales lubricantes para ser usados en la industria. Por este motivo se ha estudiado el uso de dispersantes, entre ellos un líquido iónico, y se han modificado químicamente cuatro nanoaditivos con el fin de lograr una buena estabilidad de los nanolubricantes. Se han obtenido nanolubricantes con una estabilidad temporal de hasta 11 meses.

Para diseñar nuevos lubricantes es importante examinar como la adición de los nanoaditivos influye en sus propiedades termofísicas, ya que éstas afectan al rendimiento del lubricante. Por este motivo, se han estudiado la densidad y viscosidad a presión atmosférica de los aceites base y de los nanolubricantes diseñados. Se ha cuantificado el efecto de la concentración de tres tipos de nanopartículas en los valores de estas propiedades termofísicas para nanolubricantes basados en dos aceites base.

Para la aplicación técnica de los nanolubricantes es fundamental conocer su comportamiento tribológico. Esta Tesis se ha centrado principalmente en desarrollar ensayos tribológicos para determinar el coeficiente de fricción, el espesor del film, así como analizar el desgaste producido durante estos ensayos. Para obtener la fricción se han empleado hasta cuatro equipos tribométricos diferentes y para cuantificar el desgaste producido, un

perfilómetro Óptico 3D. Se han obtenido reducciones de fricción y de desgaste (ancho de huella) de hasta 36% y 67%, respectivamente. Se han estudiado los mecanismos de reducción de desgaste de las nanoaditivos mediante microscopía electrónica de barrido y microscopía Raman confocal, entre otras.

Palabras clave: nanolubricantes, aceites base, nanopartículas, nanomateriales, líquidos iónicos, aditivos, fricción, desgaste, espesor del film, propiedades termofísicas.

USC
UNIVERSIDADE
DE SANTIAGO
DE COMPOSTELA

RESUMO

Os avances tecnolóxicos en materia de lubricación son esenciais para mellorar a mobilidade, durabilidade ou a eficiencia da maquinaria, así como para reducir as emisións de dióxido de carbono. Por outro lado, considérase que a nanotecnoloxía desenrolará un papel de liderado nos avances tecnolóxicos do século XXI. Diversas publicacións xa demostraron que os nanoaditivos poden reducir a fricción e/ou o desgaste en sistemas mecánicos. Así, combinando ambos campos, o obxectivo principal desta Tese Doutoral é deseñar e caracterizar nanolubricantes formados pola adición de nanomateriais en diferentes aceites base. En concreto, esta Tese Doutoral céntrase no estudio tribolóxico e termofísico de lubricantes formados por aceites base (ésteres e polialfaolefinas) e diferentes nanomateriais en forma de aditivos. Para tal fin, empregáronse nanoplaquetas de grafeno, nanoláminas de óxido de grafeno reducido e nanopartículas de nitruro de boro hexagonal, de magnetita de distintos tamaños (6.3 y 10 nm), así como dunha aliaxe de neodimio. Tanto os aceites base como as nanoaditivos foron caracterizados mediante numerosas técnicas.

Levouse a cabo unha profunda análise da estabilidade de todos os nanolubricantes estudados por diferentes métodos, observando que este é o principal problema para conseguir potenciais lubricantes para ser empregados na industria. Por este motivo estudouse o uso de dispersantes, entre eles un líquido iónico, e modificáronse químicamente catro nanoaditivos co fin de lograr unha boa estabilidade dos nanolubricantes. Obtivéronse nanolubricantes cunha estabilidade temporal de ata 11 meses.

Para deseñar novos lubricantes é importante examinar como a adición dos nanoaditivos inflúe nas súas propiedades termofísicas, xa que estas afectan ao rendemento do lubricante. Por este motivo, estudáronse a densidade e a viscosidade a presión atmosférica dos aceites base e dos nanolubricantes deseñados. Tamén se cuantificou o efecto da concentración de tres tipos de nanopartículas nos valores de estas propiedades termofísicas para nanolubricantes baseados en dous aceites base.

Para a aplicación técnica dos nanolubricantes é fundamental coñecer o seu comportamento tribolóxico. Esta Tese centrouse principalmente en desenrolar ensaios tribolóxicos para determinar o coeficiente de fricción, o espesor do filme, así como analizar o desgaste producido durante estes ensaios. Para obter a fricción empregáronse ata catro equipos tribométricos diferentes e para cuantificar o desgaste producido, un perfilómetro Óptico 3D. Obtivéronse reducións de fricción e de desgaste (ancho de pegada) de ata 36% y

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

67%, respectivamente. Tamén se estudaron os mecanismos de redución do desgaste dos nanoditivos mediante microscopía electrónica de varrido e microscopía Raman confocal, entre outras.

Palabras chave: nanolubricantes, aceites base, nanopartículas, nanomateriais, líquidos iónicos, aditivos, fricción, desgaste, espesura de filme, propiedades termofísicas.

USC
UNIVERSIDADE
DE SANTIAGO
DE COMPOSTELA

AGRADECIMIENTOS

Me gustaría agradecer la incesante ayuda y apoyo recibido, tanto en el ámbito profesional como personal, a lo largo de la realización de esta Tesis Doctoral por parte de mis directoras, la Prof. Josefa Fernández Pérez y la Prof. Enriqueta López Iglesias. Sin vuestros conocimientos, empeño y tiempo este trabajo no se podría haber llevado a cabo.

A la Prof. María Pérez Comuñas por la gran ayuda recibida por su parte así como por su gran empatía, porque sin serlo a veces también ha ejercido de tutora.

Al personal del servicio de la Red de Infraestructuras de Apoyo a la Investigación y al Desarrollo Tecnológico (RIAIDT) de la Universidad de Santiago de Compostela por su capacidad y dedicación a la hora de caracterizar las muestras, especialmente a la unidad de IR-Raman.

Es un placer agradecer la inestimable colaboración, en el marco de la Asociación Estratégica de Materiales de la Universidad de Santiago de Compostela AEMAT (AGRUP2018/08, Xunta de Galicia), de D. Manuel Antonio González Gómez, Dra Susana Yánez, Dra. Yolanda Piñeiro y Prof. José Rivas, todos ellos miembros del grupo Nanomag de la Universidad de Santiago de Compostela, por la síntesis y caracterización de las nanopartículas superparamagnéticas así como por su gran ayuda.

Al Prof. Diego Peña del CIQUS y del Departamento de Química Orgánica de la Universidad de Santiago de Compostela por permitirme amablemente el uso de su Laboratorio para la síntesis de rGO y sus continuos consejos, y especialmente a la Dra. Fátima García, también del CIQUS, por su valiosa asistencia en la síntesis.

Al Prof. Alfredo Amigo del Departamento de Física Aplicada de la Universidad de Santiago de Compostela) por permitirme amablemente utilizar su laboratorio, y por su ayuda con el refractómetro y el densímetro.

I want to thank Prof. Seabra, Drs. David Gonçalves, Pedro Marques and their research group (Carlos, Joao, Ramiro and Beatriz) from the Faculdade de Engenharia da Universidade do Porto (FEUP) and the Institute of Science and Innovation in Mechanical and Industrial Engineering (INEGI) for their support, assistance and good moments during the research stay in Porto. Especially to David, for all the good times, for showing me the city and his advices in the gym.

Al Prof. Luis Lugo, al Dr. Javier Vallejo, a Jose Iglesias y todo su grupo de investigación por su caluroso recibimiento durante mi corta estancia en la Universidad de Vigo. Especialmente a Javi por esas cañas y consejos tanto en lo personal como profesional.

Al grupo NaFoMat, especialmente a Pepi, María y Pablo por todos esos cafés que han hecho estos años más amenos. Al proyecto infructuoso de Boom (Jujo, Damián y Chus) por su tremendo sentido del humor, por tantos vaciles entre nosotros y por hacerme esta tesis mucho más llevadera.

A María Herrero por su enorme ayuda con el perfilómetro, así como su gran sentido del humor. A Ezequiel Vázquez por su gran labor en el Raman y su paciencia.

A Chus porque ha sido mi gran pilar en la facultad durante estos tres años, gracias por ser mi amiga, por sacarme siempre una sonrisa, por esos momentos en el gimnasio, en las comidas, tomando algo y sobre todo por ser tan auténtica. A Félix, por toda su sabiduría tanto en lo profesional como en el fitness y por darme siempre estupendos consejos. A mis compañeros de investigación Khodor y Fátima, por los buenos momentos así como la ayuda recibida durante este último año. A Ana Rama por compartir tan buenos momentos durante sus prácticas así como por los pasillos de la facultad. A Conchi por sacarme siempre una sonrisa en la cafetería y fuera de ella, por su gran sentido del humor y por ser tan natural.

A todos mis amigos de Ordes por hacerme desconectar de la tesis y por hacerme pasar siempre grandes momentos. A Xiao por todos esos consejos, por hacerme la estancia en Porto más llevadera y por todas esas risas, charlas de fútbol y buenos momentos vividos.

Y por supuesto, a mi familia: a mis padres por su gran comprensión y apoyo, por su enorme esfuerzo para que pudiese llegar aquí y por ser el espejo en el que debo mirarme cada día. A mi hermano y a mi abuela por su ayuda y comprensión incondicional. A mi ahijada Valentina, por poder verla crecer y sacarme siempre sonrisas y buenos momentos.

Gracias a todos y a cada uno de vosotros, por contribuir a que esta Tesis fuese posible.

Financiado por: FEDER/Ministerio de Ciencia, Innovación y Universidades – Agencia Estatal de Investigación/ _Proyecto (ENE2017-86425-C2-1/2-R).

Financiado por: FEDER/Ministerio de Economía y Competitividad/ _Proyecto (ENE2014-55489-C2-1/2-R).

A la Xunta de Galicia por la financiación concedida a través del programa PRINCIPIA, así como del programa IACOBUS que financió la estancia en la Universidad de Oporto (Portugal).

También agradecer a Croda, Repsol, Enel Green Power y Nanoinnva Technologies por proporcionarnos los aceites y nanopartículas.

INDEX

1. INTRODUCTION 1
   1.1. Lubricants 2
   1.2. Nanoparticles as additives 10
   1.3. Ionic Liquids as additives 15
   1.4. Background of this PhD Thesis 16
   1.5. Objectives of this PhD Thesis 18
   1.6. Structure of this work 18
   1.7. Bibliography 19
2. MATERIALS and METHODS 25
   2.1.Selection of Base oils and nanoparticle 25
   2.2. Characterization techniques 30
   2.3. Preparation of Nanodispersions 36
   2.4. Nanodispersions Stability 39
      2.4.1. Possible ways to enhance the nanodispersions stability 40
      2.4.2. Evaluation of Nanofluids Dispersion Stability 40
   2.5. Thermophysical Characterization 43
      2.5.1 Anton Paar Stabinger SVM 3000 viscometer 43
      2.5.2. Anton Paar DSA 5000 densimeter 44
      2.5.3. Anton Paar rheometer Physica MCR 101 45
   2.6. Tribological Characterization 46
      2.6.1. Tribo-cell coupled with Anton Paar rheometer 46
      2.6.2. CSM Standard Tribometer 48
      2.6.3. EHD2 Ultra Thin Film Measurement System 49
      2.6.4. Rolling bearing test rig 51
      2.6.5. 3D Optical Profilometer Sensofar S Neox 51
   2.7. Bibliography 53
3. RESULTS and DISCUSSION 55
   3.1. Publications derived directly from this PhD Thesis 55
   3.2. Communications presented at scientific conferences 57
   3.3. Complementary publications 58
   3.4. Thermophysical and tribological properties of dispersions based on graphene and a trimethylolpropane trioleate oil 61

3.5. Tribological and Thermophysical Properties of Environmentally-Friendly Lubricants Based on Trimethylolpropane Trioleate with Hexagonal Boron Nitride Nanoparticles as an Additive 63
3.6. Tribological properties of dispersions based on reduced graphene oxide sheets and trimethylolpropane trioleate or PAO40 oils 65
3.7. Synergy between boron nitride or graphene nanoplatelets and tri(butyl) ethylphosphonium diethylphosphate ionic liquid as lubricant additives of triisotridecyl trimellitate oil 67
3.8. Tribological behavior of nanolubricants based on coated magnetic nanoparticles and trimethylolpropane trioleate base oil 69
3.9. General Discussion 71
4.0. CONCLUSIONS and PERSPECTIVES 75
APPENDIX 81

USC
UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

1. INTRODUCTION

Nowadays, energy demands are continuously increasing, with a special concern for the environment and climate change. The world energy consumption in 2014 was 396 EJ (9425 Mtoe) for different uses such as industrial activity (29%), transport (28%), residential consumption (34%) and raw materials (9%) [1]. It is well known that there are large amounts of energy losses in the aforementioned energy sectors, most of them in mechanical elements of machines and vehicles, mainly due to friction and wear. Friction consumes one-fifth of all energy used worldwide and approximately one-third of all energy utilized in transport goes towards overcoming friction [2]. Tribology is the science that studies friction and wear during contact between solid surfaces in motion. There are currently several studies [2,3] which conclude that tribology plays a fundamental role in reducing global energy consumption. Controlling friction and wear losses by using new tribological solutions would reduce energy consumption substantially. These reductions also lead to longer machine lifetimes and a reduction in greenhouse gas emissions. Given this perspective, options such as the lubrication at the interface of the mechanical parts of the machines can substantially reduce energy consumption. Lubrication has been considered one of the most efficient procedures to save energy and increase the efficiency of machines used in different types of industries [4-6]. Thus, lubrication is the technique used to reduce friction and wear between two surfaces which are moving at a very short distance from each other, through the interposition of a substance called lubricant. In this situation, a slippery film is formed that minimizes friction and wear between the surfaces in contact. Besides, lubricants have other functions such as increasing cooling and heat transfer, reducing vibration and noise as well as the self-cleaning of the lubricated mechanical elements themselves [1,4]. The viscosity of the lubricant, applied load, sliding speed and temperature are the most important factors in choosing the right lubricant, since if an inappropriate lubricant is used, important energy losses can occur, due to wear and other factors such as higher energy consumption of the machine [7,8]. Currently, with continuous developments in technology, smaller mechanical devices operating in more extreme conditions, mainly critical conditions of temperature and pressure, are increasingly available. For these reasons it is necessary to develop new lubrication technologies which improve anti-friction and anti-wear properties for these systems, in order to minimize energy losses [9]. Given this need to improve the tribological properties of lubricants, the inclusion of nanoparticles as lubricant additives is a possible solution. From this point on, *lubricants containing nanoparticles as additives will be referred to as nanolubricants*. Several studies show that the use of nanoparticles as additives in lubricants have promising effects on the reduction of friction and wear in various sectors such as: automotive, industrial applications or mining [10-13]. Nevertheless, nanoparticles still present too many problems which limit their use in real applications in the industry [14]. The main problem of nanolubricants is their poor long-term stability. Thus, a deeper knowledge about the mechanisms that cause the reduction of friction and wear is needed. Furthermore, it is important to study the effect that the nanoadditives have on oil properties such as viscosity or density, since it would be ideal to retain these properties after adding the nanoparticles. The viscosity significantly influences the sealing effect and the oil consumption rate and optimizes the starting and operating requirements of the machines under variable temperature conditions. Therefore, a large alteration of this property can cause numerous failures in the system.

1.1. LUBRICANTS

As indicated above, a lubricant is a substance introduced between solid surfaces in mutual contact in order to reduce friction and wear. Therefore, a lubricated tribological system consists of two moving surfaces under a load with the presence of a lubricating agent between them. Lubrication is achieved thanks to the physical and chemical properties of the lubricating fluid. The lubrication also has the following purposes: to avoid corrosion, participate in the thermal equilibrium of the machines (the mechanical energy lost by friction dissipates in the form of heat and is practically unrecoverable), to eliminate, by circulation, impurities that can accelerate wear and reduce vibrations and noise [15]. The lubrication conditions that occur in the lubricated systems can vary significantly depending on several parameters. Therefore, it is very interesting to know how the friction coefficient varies with the viscosity of the lubricant (η), the applied load (N) and the sliding speed, (v). Depending on the thickness of the lubricating film, several types of lubrication regimes can be found [16-19]: boundary (BL), mixed (ML), elastohydrodynamic (EHL) and hydrodynamic lubrication (HDL). A Stribeck curve (Figure 1.1) describes these regimes according to the sliding speed and the applied load.

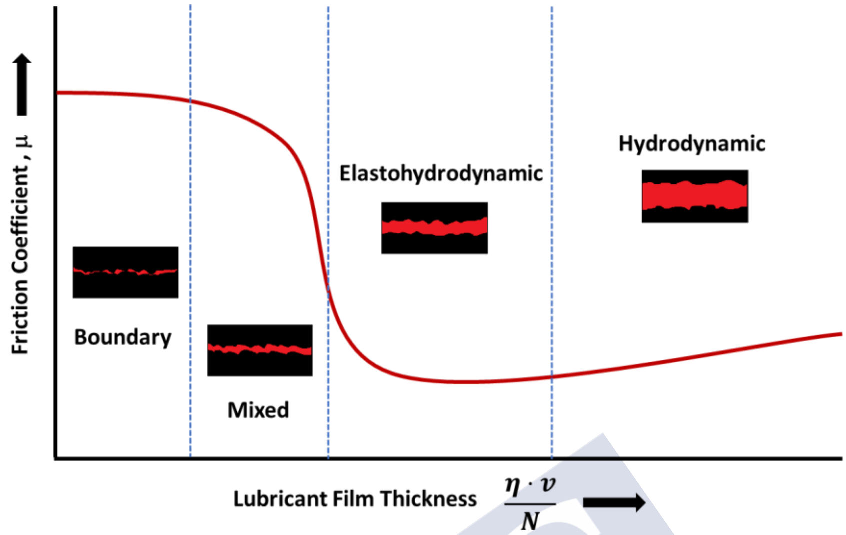


Figure 1.1 Stribeck curve showing the dependence of the friction coefficient with film thickness.

The parameter regularly used to characterize these regimes is the ratio of the minimal film thickness (*h*) to the roughness (*Ra*) [15]. In the HDL regime (*h*>> *Ra*), the fluid film is thick enough to keep the asperities of the lubricating surfaces separate. This regime occurs under conditions of low load or high speed (or high viscosity). The EHL regime takes place by decreasing the sliding speed or viscosity, or by increasing the load. The separation between the contact surfaces will be thinner than in the previous case. With small separations between the contact surfaces, the pressure in the lubricating film becomes so high as to produce an elastic deformation of the roughness, which avoids solid-solid contact and therefore wear. Moreover, in this regime the minimum friction value is reached. This regime is the one that must take place in gears in operation and in motors, among others. The maximum pressure the surfaces supports is between 0.5 and 4.0 GPa, while film thickness is lower than 1 µm. The ML regime, h ~ Ra, is transitional between the boundary and hydrodynamic regimes, when the full-lubricated (separated) and contacted (unseparated) surface areas equally influence the friction and the film parameters. Friction losses can vary over a wide range due to the two limiting regimes involved. The BL regime, *h*< *Ra*, occurs when the fluid film is not continuous and does not avoid direct contact between high points of the opposite surfaces. This boundary film lubrication occurs whenever a mechanism starts or stops. In this type of lubrication, the chemical structure of the lubricant is more important than its viscosity.

A lubricant is a multicomponent mixture of different lubricant bases and additives (antiwear, antioxidants and defoamers, among others) in a ratio of approximately 90% base and 10% additives [20]. Based on the chemical structure, base oils are generally classified into three categories: mineral, synthetic, and vegetable oils.

Mineral oils are mixtures of liquid hydrocarbons obtained from crude oil by different methods of distillation and refining [21-23]. Mineral oils are both the most broadly used lubricants (about 95% of all lubricants come from mineral oils) and the most economical lubricants. These types of oils have complex structures with a wide molecular weight, ranging from 250 g/mol (for low-viscosity lubricants) up to 1000 g/mol (for high-viscosity lubricants). Apart from liquid hydrocarbons they also contain impurities of sulphur, oxygen, and nitrogen compounds. Thousands of different organic compounds have been identified in the composition of crude oil, but the composition of most types of mineral oils is relatively uniform [23]. Depending on the chemical structure of the predominant components, mineral oils are classified into paraffinic (linear or ramified saturated hydrocarbons) or naphthenic (cycloparaffinic hydrocarbons). Paraffinic oils are the most widely used oils in lubrication due to their greater oxidation stability, higher pour point, lower volatility or higher viscosity index compared to naphthenic oils. The American Petroleum Institute (API) also classify mineral oils as: group I, group II and group III depending on the size and type of the hydrocarbon petroleum cuts. Group I oils are refined by using solvents, which is the simplest process to refine, making them the least refined and consequently also the cheapest base oils available. Group II base oils are obtained by hydrocracking, breaking up large hydrocarbon molecules into smaller ones. Most of the hydrocarbon fragments of these oils are saturated, which provide them with good antioxidant properties. Finally, Group III oils are obtained through a more severe hydrocracking process (high pressure and temperature). This process allows for the procurement of a much-refined base oil without both aromatic components and heteroatoms.

Synthetic oils (Figure 1.2) are lubricants obtained by chemical synthesis in which carbon and hydrogen compounds are combined. These oils can provide superior performance to traditional mineral based oils due to the ease of reaction control, and consequently, the desired properties of the lubricant for a specific application. They combine low volatility and high thermal stability characteristics which often affect longer service life and therefore benefits the environment. Moreover, they can reduce deposit formation as a result of good high-temperature oxidation stability. Generally, synthetic lubricants are around 4 to 8 times more expensive than mineral oils. According to chemical structure, synthetic lubricants can be broadly classified in polyalphaolefins (PAO), synthetic esters and polyalkyl glycols (PAGs) among others [22].

PAOs are the most popular synthetic lubricants and are classified into Group IV of API base oils. These types of lubricants are manufactured by polymerization of hydrocarbon molecules (α-olefins) between six to twelve carbon atoms, in the presence of a catalyst. Furthermore, with different catalytic processes, it is possible to produce tailor-made PAOs and consequently control the properties of the products, such as viscosity or the viscosity index. For example, low viscosity PAOs are synthetized by oligomerization catalyzed by BF_3 used in conjunction with a protic co-catalyst such as water or an alcohol, whereas high viscosity PAOs are produced through Ziegler-Natta reaction or organic chlorides catalysts such as aluminum alkyl compounds, in conjunction with an organic halide [24-27]. PAOs are classified and marketed depending on their kinematic viscosity at 373.15 K which has to fall within a specific bracket for each PAO grade [26]. They have excellent thermal properties, high viscosity index (VI) values, indicating small changes in viscosity as the temperature varies. Besides, PAOs are also characterized by having low volatility and high oxidative stability [26]. These oils are principally used as a base oil in the automotive and gear industry as well as in hydraulic fluids for automatic transmissions [27].

Synthetic esters are obtained through a condensation reaction of one or more acids and an alcohol. The high polarity of these bases shows some interesting properties in a lubricant such as good thermal stability, low volatilities, low vapor pressures. From an environmental perspective, they are very interesting since they can have excellent biodegradability, as well as low toxicity [28]. In addition, sometimes esters can be mixed with PAOs with the aim of improving the solubility of the additives. Ester content varies from 5 to 25% wt depending on the ester and the desired properties.

Monoesters are obtained through a reaction of monofunctional acid with a monofunctional alcohol, therefore they have low molecular weight and high volatility.

Diesters are formed by the reaction of a polyacid with a monofunctional alcohol. Among other diesters, trimellitates are an important group of aromatic esters. In this case trimellitates are synthetized by esterification of a monofunctional alcohol with a trimellitic anhydride [27]. The main advantages of trimellitate esters are good thermal stability, good stability to oxidation, high film strength, good low temperature properties, and good hydrolytic stability. They also present a broad viscosity range and a low volatility because of their high molecular weight. Trimellitates are applied in the automotive industry where resistance to high temperature is required and they are also used in refrigeration air compressors and aviation [22,29].

Polyol esters are produced by the reaction of a polyfunctional alcohol with one or more monofunctional acids. These type of lubricants are widely used in the refrigeration of air compressors, aviation, metalworking and biodegradable hydraulic fluids [22]. Some polyol esters are synthesized by the reaction of a vegetable oil with a polyfunctional alcohol, which leads to a biodegradable ester. Vegetable oils as lubricants are not good due to inadequate oxidation stability, poor low temperature properties or hydrolytic stability. In order to eradicate these negative properties, a good way is to convert these oils to natural synthetic esters through structural modifications [30,31]. The formed biodegradable ester might have better pour point, thermal and oxidative stability properties but could present inferior viscosity, VI and biodegradability. Monoesters, diesters, polyol esters and trimellitates are classified in group V of the API, which includes all base oils that do not belong to groups I to IV.

Another type of synthetic oils is *polyalkylene glycols* (PAGs). These oils are synthesized by reacting an alcohol (initiator) with one or more alkylene oxides (propylene oxide or ethylene oxide) under alkaline conditions and elevated temperatures, resulting in homo and co-polymers as products [22]. Propylene oxide provides water insolubility whereas ethylene oxide provides water solubility. In this type of oils molecular weight and viscosity can be controlled during the synthesis step. PAGs usually have high viscosity rates, low fluidity points as well as good lubricity. These base oils are commonly used as gear and chain oils as well as in hydraulics and gas compressor systems.

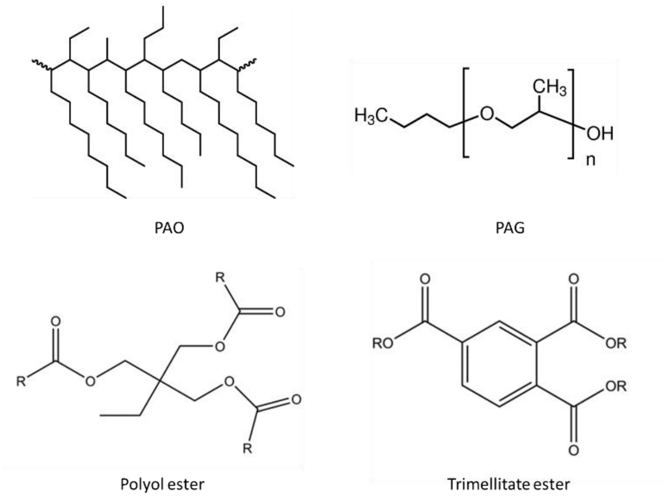


Figure 1.2 Chemical structure of some synthetic oils.

Finally, *vegetable oils* basically consist of triglycerides, naturally synthesized by the esterification of a tri-alcohol, called glycerol, with three fatty acids [32,33]. Vegetable oils are an environmentally friendly alternative to mineral oils because they are biodegradable. Some advantages such as high lubricity, appropriate viscosity–temperature behavior and low lubricant consumption appear in these types of lubricants. Lubrication properties of vegetable base oils are similar to those of mineral oils. On the other hand, the main disadvantages of vegetable lubricants are their low oxidation (form acidic products), temperature stabilities and they get hydrolyzed easily in the presence of humid air or in aqueous medium [34]. Vegetable oils with high oleic contents are the best alternative for substituting conventional mineral oils and synthetic esters. Vegetable oils are commonly used in industrial applications such as hydraulic oils, refrigeration oils or engine oils.

Generally, base fluids (mineral, synthetic or vegetal) cannot satisfy all the requirements of high-performance lubricants without the benefit of modern additive technology [35]. The *additives* are compounds of organic or inorganic nature which are dissolved in the base oil in concentrations of up to 10-20 wt%. Some additives provide new and beneficial properties to the lubricant, some improve properties already present, while others reduce the rate at which some undesirable changes take place during the service life of the lubricating oil [35,36]. Each additive is selected for its ability to perform one or more specific functions in combination with other additives. Selected additives are formulated into packages for use with a specific lubricant base stock and for a specified end-use application.

The major functional additive types are: dispersants, detergents, oxidation inhibitors, antiwear or antifriction agents, extreme-pressure additives, and viscosity index improvers [36-38]:

-*Antioxidants:* Oxidation is the attack on the weakest components of the base oil by oxygen in the air. Oil oxidation is a set of chemical reactions initiated and propagated by reactive chemicals formed within the oil called free-radicals. Several antioxidant additives neutralize the free-radicals that cause oxidation while others trap free-radicals. These are sacrificial additives that are consumed while performing the work of preventing oxidation, thus protecting the base oil. Over time, these additives reduce to the point where they can no longer be effective. They are present in engines, turbines, gears oils and hydraulic fluids [39].

-*Corrosion Inhibitors*: These additives are chemical compounds that decrease the corrosion rate of a material. Corrosion inhibitors are essential in the presence of water because it accelerates the corrosion of metal. Rust inhibitors are usually compounds that have a high polar attraction toward metal surfaces. By physical or chemical interaction on the metal surface, they form a tenacious, continuous film that prevents water from reaching the metal surface. Similar to the previously mentioned additives, corrosion inhibitors are common in engines, turbines, gears oils and hydraulic fluids [40].

-*Dispersants and Detergents:* Dispersants are mainly found in engine oil along with detergents to keep engines clean and free of deposits caused by sedimentation of other additives. Therefore, the main function of these additives is to keep the lubricant particles dispersed or suspended in the oil [41].

-*Viscosity Index Improvers:* these types of additives are large polymers that decrease the loss of viscosity when the temperature increases. On the other hand, these additives also improve the oil flow at low temperatures, resulting in wear reduction. These additives are widely used in multi-grade engine oils [38,42].

-*Pour Point Depressants (PPD)*: The pour point of a liquid is the temperature below which the liquid loses its flow characteristics. When cooled to low temperatures, lubricant oils suffer some changes such as solidification, solidification with formation of a precipitate of macrocrystals and solidification with the formation of microcrystals which swell to give a crystalline structure trapping the remaining oil [43]. This causes lubrication failure and leads to serious damage to machine elements. A pre-heating system can avoid the problem, but it consumes considerable time and energy. Pour point depressants are additives used to lower the pour point of an oil by modifying the structure of wax crystals. PPD additives do not entirely prevent wax crystal growth, but rather lower the temperature at which a rigid structure is formed. These additives are used for hydraulic fluids [44,45]

-*Friction modifiers (FM)*: These additives are polar molecules combined that minimize light surface contacts (sliding and rolling) that may occur in a given machine. FM modifiers, also named film-forming additives, are added to lubricants to reduce friction in boundary and mixed lubrication regimes. There are some kinds of FM additives such as organic friction modifiers (OFMs), dispersed nanoparticles or functionalized polymers. Friction modifiers are typically used in engine oils and automatic transmission fluids to alter the friction between engine and transmission components [41,46].

-*Anti-wear additives (AW)*: AW additives chemically react with the metal surface to be protected, forming a lubricious coating that preserves the metal from wear under boundary lubrication conditions. These additives create a surface that is harder than the unprotected base metal. Some of the more effective antiwear additives have been zinc-containing additives or ashless phosphorus-based additives. Zinc dialkyl dithiophosphate (ZDDP) has been successfully used as an antiwear additive for decades in a multitude of applications including engine oils, hydraulic oils, and circulation oils [40,47].

-*Extreme Pressure Additives (EP)*: These materials are required to reduce friction, control wear, and prevent severe surface damage at high temperatures or under heavy loads where more severe sliding conditions exist. Localized high temperatures are the result of rubbing between opposing surface asperities and the breaking of junctions between these asperities. These nanoadditives chemically react with the sliding metal surfaces to form relatively oil insoluble surface films which prevent soldering and adhesion. Some authors consider that EP is an older terminology and these additives are also AW additives. These additives are used in gear oils [40, 48].

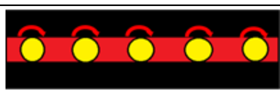
Spikes [49] published a review of friction modifier additives that are commonly used in lubrication. In recent years the interest of using solid particles of small size (1 to 500 nm) as both friction and wear reduction additives has been growing [50]. In recent years ionic liquids (ILs) are also being investigated as anti-friction and anti-wear additives for lubricants, alone or in combination with different types of nanoparticles [51-54].

1.2. NANOPARTICLES AS ADDITIVES

Nowadays, traditional lubricants have reached their performance limits. Thus, new lubricant formulations which can achieve high energy efficiency under severe conditions must be developed. Currently, the development of nanotechnology in this sector is notable, as evidenced by the numerous researchers who use nanoparticles as anti-friction and anti-wear additives [50, 55]. There are many reasons for use of nanoparticles as a lubricant additive but most importantly is their small size, which allows nanoparticles to enter in the contact area, resulting in a positive lubrication effect [56]. One of the advantages of using nanoparticles as lubricant additives is their low volatility which avoids losses at high temperature conditions [49]. Moreover, the appropriate nanoparticles used as additives must be less chemically reactive than common additives since their films are formed mechanically, so they will be more durable and less reactive with other additives [49]. As shown in Table 1.1, nanoparticles as friction modifiers additives can work by different lubrication mechanisms: rolling effect and tribo-film formation owing to direct effect of the nanoparticle on the surface and mending and polishing effects due to surface enhancement [57].

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Table 1.1 Lubrication mechanisms of nanoparticles as additives [58,59].

Mechanism	Description	
Rolling	Spherical nanoparticles roll between the two sliding surfaces.	
Tribo-film	Nanoparticles form a protecting film that protects the surrounding surfaces.	
Mending	Nanoparticles fill the cracks and repair microdamages on rubbing surface.	
Polishing	Hard nanoparticles polish the rubbing surfaces.	

According to several factors such as size, morphology or physical and chemical properties, nanoparticles can be widely classified in different types. As regards the chemical structure, nanoparticles as lubricant additives are mainly classified into several categories [10]: carbon-based nanomaterials, metals, metal oxides, ceramics, rare earth compounds, composites, among others. Dai *et al.* [10] reviewed the lubrication mechanisms for numerous nanoparticles of different types in oils.

The *carbon-based nanomaterials* group is made up of graphene, graphene nanoplatelets (GnP), carbon nanotubes, fullerenes, nanodiamonds among others [60]. These nanomaterials are formed mainly by carbon. Due to its allotropic characteristics, carbon forms compounds with different properties depending on the arrangement of the adjacent carbon atoms. Carbon materials have much interest in the field of tribology due to their high chemical stability and excellent mechanical, thermal, chemical and electrical properties. Graphene is a nanomaterial organized in a two-dimensional layer of carbon atoms with sp^2 hybridization that are linked in a hexagonal lattice structure. GnPs are carbon nanostructures consisting of small stacks of graphene sheets which have a thickness ranging from 1 nm to a few tens of nanometers, and lateral linear dimensions which vary from a few micrometers up to hundreds of micrometers. Carbon nanotubes are structures with diameters of few nanometers that form one-dimensional structures since the length is orders of magnitude larger than their diameter. They have different properties from other carbon materials, with unique mechanical and electrical properties. Fullerenes have an icosahedral structure that is generally composed of 20 hexagons and 12 pentagons (C_{60}) in which each carbon atom is linked to 3 other carbon atoms with sp^2 hybridization [61]. It should be mentioned that the two-dimensional structures of graphene exhibit higher lubrication ability than other carbon nanostructures, such as nanotubes or fullerenes [62].

As pure carbon-based nanomaterials are quite expensive, other similar materials containing not just carbon but also oxygen and hydrogen are being studied as lubricant additives. Graphite oxide is formed by carbon, oxygen, and hydrogen in variable ratios, obtained by treating graphite with strong oxidizers. This material spontaneously disperses in basic solutions or can be dispersed by sonication in polar solvents to produce monomolecular sheets, known as graphene oxide (GO). GO is used to prepare strong paper-like materials, composites, and lubricant additives among others. Moreover, it has been utilized as a precursor for large-scale production of graphene [63].

Several authors have already studied nanolubricants based on carbon-based nanomaterials. For instance, Eswaraiah *et al.* [64] have studied the tribological behavior of an engine oil with ultrathin graphene as additive, observing 80% friction reduction and 33%

wear reduction in comparison with the oil without additives. Zheng *et al.* [65] analyzed the tribological performance of PAO4 base oil with the addition of graphene nanosheets obtaining good tribological properties: 70% and 50% reduction in friction and wear respectively. In addition, Azman *et al.* [66] studied the effects of graphene nanoplatelets as additives in palm-oil trimethylolpropane (TMP) ester blended in a polyalphaolefin (PAO10), obtaining slight reductions in wear for low concentrations of GnPs. Moreover, Sarno *et al.* [67] studied the tribological behavior of GO in mineral oil from boundary and mixed lubrication to elastohydrodynamic regimes. These authors obtained that the average friction coefficient decreased by more than 20% compared with the base lubricant value. As regards wear, the average decreasing was around 30%. Khalil *et al.* [68] examined the tribological properties of two lubricating mineral oils (Mobil Gear 627 and a paraffinic), with multi-walled carbon nanotubes (MWCNTs) nanoparticles used as additives. They obtained good wear results with reductions of 68% and 39% in comparison to neat base Mobil Gear 627 and paraffinic mineral oils, respectively. Additionally, friction reductions of about 57% and 49% were achieved for both MWCNTs nanolubricants. Lee *et al.* [69] studied tribological properties of fullerene nanoparticles-added mineral oil for several concentrations. The results showed that the nanolubricant containing the higher concentration of fullerene resulted in a lower friction coefficient and less wear. Raina *et al.* [70] evaluated the effect of diamond nanoparticles on the friction and wear performance of a PAO base oil, obtaining 8% and 30% reductions in friction coefficient and wear, respectively.

Metal nanoparticles are important in nanoscale science due to their unusual physical and chemical properties such as special thermal, electronic, magnetic, optical, chemical and catalytic properties [71]. The use of metallic nanoparticles as oil additives can improve their anti-wear properties, especially at extreme pressures [72]. There are several studies in which some metallic nanoparticles have been applied as lubricant additives, including Ni, Al, Cu, Fe, Zn, Co and Pb, among others [59,73,74]. Viesca *et al.* [72] studied the tribological behavior of adding coated and non-coated copper nanoparticles to a polyalphaolefin (PAO6). These authors concluded that all nanolubricants decreased wear in comparison with PAO6 (between 10% and 50%) under mixed lubrication regime but not in extreme pressure conditions. Padgurskas *et al.* [73] analyzed the effect of adding Fe, Cu and Co nanoparticles in a mineral oil (SAE10) and their tribological performance. The tests showed that all combinations of nanoparticles significantly reduced the friction coefficient and wear, being the best behavior for Cu nanoparticles. Recently, Flores-Castañeda *et al.* [75] used bismuth nanoparticles as additives of mineral base oils observing that friction coefficient and the wear rate decrease with an increasing concentration of the nanoparticles.

Metal oxide nanoparticles are formed by copper, iron, zirconium, zinc or titanium oxides among others. Wu *et al*. [76] have discussed the tribological properties of two lubricating oils (an API-SF engine oil and a base oil) with CuO, TiO_2, and Nano-Diamond nanoparticles used as additives. They observed that all nanoparticles, especially CuO, added to standard oils show good friction-reduction and anti-wear properties, being the best reductions over 20 and 80% for friction and wear, respectively. Moreover, Hernández Battez *et al.* [77] have analyzed the tribological performance of CuO, ZrO_2 and ZnO nanoparticles as antiwear additives in a polyalphaolefin (PAO6) base oil. They found that all nanolubricants reduce the friction coefficient and wear in comparison with PAO6. Alves *et al.* [78] studied the tribological performance of tiny coated CuO nanoparticles (5 nm) as EP additives of a PAO oil (0.1, 0.25 and 0.5 wt%) using toluene as dispersant, finding the best reduction in the friction coefficient and wear for the lowest concentrated nanolubricant. Magnetites (Fe_3O_4) are specific oxides which have magnetic properties. Zhou *et al.* [79] have studied the tribological behavior of coated Fe_3O_4 nanoparticles as additives of liquid paraffin base oil. These authors observed that both coefficient of friction and wear are reduced with the increase of concentrations of Fe_3O_4 nanoparticles. Recently , Zhang *et al.* [80] analyzed the tribological behavior of PAO6 with graphene oxide/Fe_3O_4 as additives obtaining reductions of 7% and 52% in friction and wear, respectively, in comparison to the base oil.

Nanoceramics are a nanoparticle type composed of ceramics, which are solid materials comprising an inorganic compound of metal, non-metal or ionic and covalent bonds manufactured by heat treatment. Nanoceramics particles have unique properties due to their size and molecular structure. There are several studies of using nanoceramics as lubricant additives. Among them, Wei *et al.* [81] studied the tribology properties of Al_2O_3 nanoparticles as lubricating oil additives, observing that Al_2O_3 nanoparticles can effectively reduce friction coefficient and the wear scar diameter in comparison with the base oil. Peng *et al.* [82] have investigated the tribological properties of liquid paraffin with SiO_2 nanoparticles as additives. These authors observed better tribological properties for SiO_2 nanolubricants than for pure paraffin oil. Moreover, Cortes *et al.* [83] studied the tribological characteristics of sunflower oil modified with silicon dioxide (SiO_2) and TiO_2 nanoparticles as lubricant additives at different concentrations These authors concluded that friction coefficient decreased with the addition of SiO_2 and TiO_2 nanoparticles by 77.7% and 93.7%, respectively, in comparison to sunflower oil. On the other hand, the volume loss was lowered by 74.1% and 70.1%, with the addition of SiO_2 and TiO_2 nanoparticles, respectively.

Rare earth nanoparticles are also used in lubrication. The most common elements are La and Ce, that could be either applied as lubricant additives, or be doped into other nanoparticles, such as TiO_2 [10]. Hou *et al.* [84] analyzed the tribological properties of surface-modified LaF_3 nanoparticles as additive of a fluoro silicone oil, concluding that LaF_3 nanoparticles exhibit excellent anti-wear properties as additives with wear reductions of up to 43%. Recently, Pena-Paras *et al.* [85] studied the tribological performance of polymeric lubricants dispersed with cerium oxide (CeO_2) nanoparticles as additives at extreme pressure (EP) conditions. These authors concluded that CeO_2 nanoadditives have friction-reducing and EP properties, making them suitable as lubricant additives in the metal-mechanic industry.

Other nanoparticles used in this field are *nitrides and sulfides*. One of the most used nitrides is boron nitride (BN). BN nanostructures can be obtained in different morphologies such as hexagonal (h-BN) and spherical nanoparticles. The first ones have a lamellar crystalline structure with van der Waals forces between sheets, like those of graphite or GnPs. h-BN sheets provide excellent lubrication characteristics due to the relatively weak van der Waals interactions [86]. h-BN is the softest and most lubricious polymorph of BN which has both high thermal stability and thermal conductivity as well as numerous industrial applications, especially in metalworking processes where cleanliness of the working environment is required [87]. Additionally, h-BN is an environmentally-friendly material [88]. Wang *et al.* [89] analyzed the friction properties of castor oil with the addition of h-BN nanoparticles, observing reductions of up to 30% in the friction coefficient and 50% in wear compared to the oil without additives. Xie *et al.* [90] compared the tribological behavior effects of MoS_2 and SiO_2 as additives of a mineral oil, and obtained improvements with both nanoparticles, especially for MoS_2 nanolubricants.

Nanocomposites are defined as multicomponent materials including multiple different phase domains in which at least one of the phases has dimensions of the order of nanometers. The nanocomposites most commonly used in lubrication are Al_2O_3/SiO_2, ZrO_2/SiO_2, Cu/SiO_2

and Al_2O_3/TiO_2 [10]. Li *et al.* [91] found that ZrO_2/SiO_2 nanocomposite effectively improves the lubricating properties of a base oil, obtaining reductions in both friction coefficient and wear scar around 15%. Luo *et al.* [92] analyzed the tribological properties of Al_2O_3/TiO_2 nanocomposites obtaining significant friction and wear reductions. Moreover, these authors observed that as oil additives these nanocomposites exhibit better behavior than the separated nanoparticles.

On the other hand, one of the main challenges of using nanoparticles as additives is to achieve *homogeneous and stable dispersions* along time, as can be seen in further detail in the next chapter. The problem associated with stability is due to the fact that nanoparticles tend to aggregate because of van der Waals forces and consequently sedimentation occurs [93]. So, preparation of nanolubricants is the key step to achieve a lubricant that can be used in the industry, since long-term stability is needed. In order to obtain stable suspensions of nanoparticles in lubricant oil, two strategies are used. One is incorporating dispersant with nanoparticles. For instance, Wan *et al.* [94] used Span80 as a dispersant of MoS_2 nanoparticles to ensure suspension stability and Hu *et al.* [95] studied the tribological properties of lanthanum borate nanoparticles with a dispersing agent sorbitol monostearate. The other is chemical modification of nanoparticles surface. For example, Mungse *et al.* [96] developed a chemical method for selective inclusion of long alkyl chains on the defects sites of reduced graphene oxide sheets through the amide linkage, which helps their stable dispersion in the lube oil. Chen *et al.* [13] recently reviewed the time stability of numerous nanolubricants. For this task, these authors analyzed different characteristics of nanoparticles such as material nature, particle size, and surface modification, concluding that surface modification is essential to disperse nanoparticles into a lubricating oil.

1.3. IONIC LIQUIDS AS ADDITIVES

Ionic liquids (ILs) are salts that consist in ion pairs of bulky asymmetric cations and weakly coordinating, more highly symmetric anions. They have melting points below 100 ºC, very low volatilities as well as high thermal and chemical stabilities [51]. Due to these outstanding properties, ILs have been tested as neat lubricants since 2001 [8,97,98]. One advantage of using ILs is to replace the traditional lubricant systems with potentially more efficient and/or more environmentally friendly alternatives [38]. Nevertheless, ILs are much more expensive than traditional base oils, so their use as neat lubricants is limited to critical

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

applications [99]. Thus, ILs can be used as lubricant additives, because small amounts of ILs would be needed to improve the tribological performance of base oils. Furthermore, the chemical structure of some ILs can also be similar to traditional base oils due to the presence of long hydrocarbon chains. This leads to good IL solubility in base oils with hydrocarbon chains as polyalphaolefins or esters. Zhou *et al.* [51] reviewed the miscibility of numerous ILs in several base oils and lubricants, finding that ILs based on phosphonium or ammonium cations and on organophosphate anions have better miscibility than other ILs. Furthermore, the lubricating behavior of ILs as additives show a strong correlation with their chemistry, concentration and compatibility with other oil additives [51]. Interestingly, oil-soluble ILs, when used as lubricant additives, have frequently showed effective wear and friction reductions in tribological tests [100-104]. Hence, the best performing ionic liquids that are miscible in non-polar base oils are the phosphonium phosphates or phosphinates.

In recent years, the idea of combining the desired properties of ionic liquids with nanoparticles as base oil additives emerged. These hybrid mixtures sometimes exhibit interesting positive synergies, however, investigations with the combined effects of ILs and nanoparticles as lubricant additives are uncommon. Amiril *et al.* [105] studied the tribological behavior of a chemically modified palm olein trimethylolpropane ester with the addition of trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate IL and hexagonal boron nitride nanoparticles, observing a slight increase in anti-wear and antifriction properties compared with the base oil. Li *et al.* [106] investigated the synergistic effects of 2-mercaptobenzothiazolate IL with molybdenum nanoparticles in a polyethylene glycol base oil obtaining good friction-reduction and anti-wear performances only at high temperatures. Senatore *et al.* [107] studied the synergies of 1-ethyl-3-methylimidazolium with graphene oxide (GO) in a polyalkylene glycol base oil, obtaining a friction reduction of 17%. Finally, Sanes *et al.* [52] studied the tribological performance of 1-octyl-3-methylimidazolium tetrafluoroborate IL and graphene as additives of two different oils, an isoparaffinic base oil and a fully formulated oil (SAE 10W30). For the former, good anti-wear results were found but for the fully formulated oil no positive synergies were observed.

1.4. BACKGROUND OF THIS PHD THESIS

This PhD Thesis was carried out in the Laboratory of Thermophysical Properties of the Applied Physics Department of the University of Santiago de Compostela and in the

Mechanical Engineering Department of the Engineering Faculty of the University of Porto and in the “Instituto de Ciência e Inovação em Engenharia Mecânica e Engenharia Industrial (INEGI)”. The Laboratory of Thermophysical Properties is integrated in the NaFoMat research group "Nanomaterials, Photonics and Soft Matter" (GI-1488). This research group has received funding from the Consellería de Cultura, Educación e Ordenación Universitaria (Xunta de Galicia) as competitive reference group (GRC ED431C 2016/001). This program gives funding to research groups which have high scientific production and R&D performance. Furthermore, the NaFoMat group took part in the Galician Strategic Grouping of Physics (AGRUP2015/11), from January 2016 to December 2018 and has participated in the Galician Strategic Grouping of Materials -AEMAT (AGRUP2018/08) since January 2019. In the framework of AEMAT we are collaborating through the internal project named “Development of nanolubricants based on functionalized 1D and 2D nanoparticles and nanomaterials (nanoLUBs)” with the NanoMag laboratory. Several tasks concerning the superparamagnetic nanoparticles involved in this PhD Thesis were performed in this laboratory. Moreover, this group is also integrated in the Galician Ionic Liquid Network which is currently in its 3rd edition (GRC ED431C 2017/22). Both groupings and the network have received funding from Xunta de Galicia.

This PhD Thesis was developed in the framework of two national research projects. The first one is called “Development of thermal fluids and lubricants based on nanoadditives for the production, storage use of energy efficient”, (NanoLuter, ENE2014-55489-C2-1/2-R, 2015-2018) and was supported by the Spanish Ministry of Economy and Competitiveness and the UE FEDER program. The aim of this project is to design and develop nanolubricants for different applications such as renewable energy and automotive mechanical systems. For this purpose, stability, thermophysical and tribological studies were carried out. The second one, entitled “Development of hybrid nanofluids, nanolubricants and nano-enhanced Phase Change Materials for the transfer, storage and production of energy”, (AdLuter, ENE2017-86425-C2-1/2-R, 2018-2020) was also supported by the Spanish Ministry of Economy and Competitiveness. Its main objective is the proposition of new advanced materials focused on the field of lubrication, storage and transfer of thermal energy guide to renewable energies (solar, wind, hydraulic and geothermal) and for automotive applications. Both projects were coordinated together with the University of Vigo.

UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

As mentioned above, part of this PhD Thesis was performed in the University of Porto, during a research stay for three months (15/03/2019 to 14/06/2019) and under the supervision of Prof. Seabra. The Interreg IACOBUS Program 2019 funded this research stay. This program focuses on encouraging cooperation between resources of the higher education institutions of the Euroregion Galicia - North of Portugal. Furthermore, some studies were carried out in a short stay at the University of Vigo at the Applied Physics department in FA2 laboratory.

1.5. OBJECTIVES OF THIS PHD THESIS

The main objective of this PhD Thesis is to design and characterize nanolubricants formed by the addition of nanoparticles in some esters and PAO base oils. For this purpose, the following specific objectives were proposed:

1. Selection, synthesis and characterization of nanoadditives to obtain suitable nanolubricants.
2. To obtain stable dispersions of nanoadditives in some synthetic lubricant bases, through chemical surface modification and the use of ionic liquids.
3. Thermophysical characterization of some nanolubricants: density, dynamic viscosity, viscosity index.
4. Evaluation of the tribological behavior (friction and wear) of designed nanolubricants in boundary lubrication regime. Influence of weight concentration and size of nanoadditives.
5. Evaluation of some nanolubricants for elastohydrodynamic lubrication: Stribeck curves, film thickness and friction torque measurements.
6. Analysis of synergies between an ionic liquid and nanomaterials as hybrid additives in the formulation of efficient lubricants

The ultimate goal of the present fundamental study is to contribute to provide knowledge on lubricants that can be used in real applications improving the currently used lubricant performance as well as proposing high performance environmentally friendly lubricants.

1.6. STRUCTURE OF THIS WORK

In accordance with the proposed objectives the following structure has been used to describe the achievements reached in this PhD Thesis and the steps followed to meet goals.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Thus, the second chapter describes the general diagram of the methodology followed in this work, the strategies to select the nanoparticles and to improve the stability time, the experimental techniques used and the most used base oils and nanoparticles as well as their main properties. Third chapter includes the full description and the general discussion of the stability results, thermophysical characterization and tribological analyses for the designed nanolubricants. Chapter four reports the conclusions and some future work propositions. An annex presents a summary of this PhD Thesis in Spanish.

1.7. BIBLIOGRAPHY

[1] K. Holmberg, A. Erdemir, Influence of tribology on global energy consumption, costs and emissions, Friction 5 (2017) 263-284.
[2] K. Holmberg, A. Erdemir, The impact of tribology on energy use and CO_2 emission globally and in combustion engine and electric cars, Tribology International 135 (2019) 389-396.
[3] M. Hassan, S. Amzar Zulkifli, H. Hasnul, A. Yusoff, Tribological advancement – strategies and effects towards emissions and global energy consumption, MATEC Web Conf. 204 (2018) 00003.
[4] G. Paul, H. Hirani, T. Kuila, N.C. Murmu, Nanolubricants dispersed with graphene and its derivatives: an assessment and review of the tribological performance, Nanoscale 11 (2019) 3458-3483.
[5] A. Vacca, Energy Efficiency and Controllability of Fluid Power Systems, Energies 11 (2018) 1169.
[6] H. Cen, Effect of lubricant ageing on lubricants' physical and chemical properties and tribological performance; Part I: effect of lubricant chemistry, Industrial Lubrication and Tribology 70 (2018) 385-392.
[7] C. Nutakor, D. Talbot, A. Kahraman, An experimental characterization of the friction coefficient of a wind turbine gearbox lubricant, Wind Energy 22 (2019) 509-522.
[8] I. Minami, Ionic Liquids in Tribology, Molecules 14 (2009) 2286-2305.
[9] H.-J. Kim, K.-J. Seo, K.H. Kang, D.-E. Kim, Nano-lubrication: A review, International Journal of Precision Engineering and Manufacturing 17 (2016) 829-841.
[10] W. Dai, B. Kheireddin, H. Gao, H. Liang, Roles of nanoparticles in oil lubrication, Tribology International 102 (2016) 88-98.
[11] K. Holmberg, P. Andersson, N.-O. Nylund, K. Mäkelä, A. Erdemir, Global energy consumption due to friction in trucks and buses, Tribology International 78 (2014) 94-114.
[12] K. Holmberg, P. Kivikytö-Reponen, P. Härkisaari, K. Valtonen, A. Erdemir, Global energy consumption due to friction and wear in the mining industry, Tribology International 115 (2017) 116-139.
[13] Y. Chen, P. Renner, H. Liang, Dispersion of Nanoparticles in Lubricating Oil: A Critical Review, Lubricants 7 (2019) 7.
[14] N.F. Azman, S. Samion, Dispersion Stability and Lubrication Mechanism of Nanolubricants: A Review, International Journal of Precision Engineering and Manufacturing-Green Technology 6 (2019) 393-414.
[15] D. Wu, Research and Development of Energy - saving and Noise-Reducing Engine Lubricants, IOP Conference Series: Materials Science and Engineering 493 (2019) 012008.
[16] R. Stribeck, Die wesentlichen Eigenschaften der Gleit- und Rollenlager, Springer (1903).
[17] R. Stribeck, Kugellager für beliebige Belastungen, Springer (1901).

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

[18] W. Chong, M. Cruz, Elastoplastic contact of rough surfaces: A line contact model for boundary regime of lubrication, Meccanica 49 (2014) 1177-1191.
[19] Y. Yan, 7 - Tribology and tribo-corrosion testing and analysis of metallic biomaterials. in: M. Niinomi, (Ed.), Metals for Biomedical Devices, Woodhead Publishing, 2010, pp. 178-201.
[20] L. Burstein, 3 - Lubrication and roughness. in: J.P. Davim, (Ed.), Tribology for Engineers, Woodhead Publishing, 2011, pp. 65-120.
[21] M.M. Khonsari, E.R. Booser, Applied Tribology: Bearing Design and Lubrication, 2nd Edition, John Wiley & Sons, 2008.
[22] L.R. Rudnick, S.Z. Erhan, Synthetic, Mineral Oils and Bio-based Lubricants, 2nd Edition. CRC Press Taylor and Francis Group, London, 2013.
[23] I.D. Marinescu, W.B. Rowe, B. Dimitrov, I. Inasaki, Tribology of abrasive machining processes, William Andrew Inc., USA, 2004.
[24] A. Voelkel, J. Fall, Chromatographic and non-chromatographic characterization of poly-α-olefins, Journal of Synthetic Lubrication 24 (2007) 91-100.
[25] Q. Huang, L. Chen, L. Ma, Z. Fu, W. Yang, Synthesis and characterization of oligomer from 1-decene catalyzed by supported Ziegler–Natta catalyst, European Polymer Journal 41 (2005) 2909-2915.
[26] J.M. Hogg, F. Coleman, A. Ferrer-Ugalde, M.P. Atkins, M. Swadźba-Kwašny, Liquid coordination complexes: A new class of Lewis acids as safer alternatives to BF_3 in synthesis of polyalphaolefins, Green Chemistry 17 (2015) 1831-1841.
[27] R. Benda, J. Bullen, A. Plomer, Synthetics basics: Polyalphaolefins — base fluids for high-performance lubricants, Journal of Synthetic Lubrication 13 (1996) 41-57.
[28] S.J. Randles, Esters. In Synthetics, mineral oils, and bio-based lubricants, CRC Press (2005).
[29] Wiley, Ullmann's Polymers and Plastics: Products and Processes, 4 Volume, W. Wiley-VCH, 2016.
[30] E. Uosukainen, Y.-Y. Linko, M. Lämsä, T. Tervakangas, P. Linko, Transesterification of trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants, Journal of the American Oil Chemists' Society 75 (1998) 1557-1563.
[31] R. Yunus, A. Fakhru'l-Razi, T.L. Ooi, S.E. Iyuke, J.M. Perez, Lubrication properties of trimethylolpropane esters based on palm oil and palm kernel oils, European Journal of Lipid Science and Technology 106 (2004) 52-60.
[32] Y. Bertrand, L.C. Hoang, Vegetal oils as substitute for mineral oils, Proceedings of the 7th International Conference on Properties and Applications of Dielectric Materials (Cat. No.03CH37417), 2003, pp. 491-494 vol.492.
[33] W.K. Shafi, A. Raina, M.I. Ul Haq, Friction and wear characteristics of vegetable oils using nanoparticles for sustainable lubrication, Tribology - Materials, Surfaces & Interfaces 12 (2018) 27-43.
[34] R. Garcés, E. Martínez-Force, J.J. Salas, Vegetable oil basestocks for lubricants, Grasas y Aceites 62 (2011) 21-28.
[35] T. Mang, Lubricants and their Market. in: W. Dresel, T. Mang, (Eds.), Lubricants and Lubrication, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2017.
[36] Lubricant Additives-A Practical Guide. https://www.machinerylubrication.com/Read/31107/oil-lubricant-additives.
[37] S.Q.A. Rizvi, A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design. ASTM International, West Conshohocken (2009).
[38] L.R. Rudnick, Lubricant Additives: Chemistry and Applications, 3rd Edition, CRC Press Taylor and Francis Group, Boca Raton, 2017.
[39] A. Kassler, E. Pittenauer, N. Doerr, G. Allmaier, Development of an accelerated artificial ageing method for the characterization of degradation products of antioxidants in lubricants by mass spectrometry, European Journal of Mass Spectrometry 25 (2019) 300-323.
[40] M. Pirro, M. Webster, E. Daschner, Lubrication Fundamentals, 3rd Edition,Revised and Expanded, CRC Press Taylor and Francis Group, Boca Raton, 2016.

[41] G. Tsagkaropoulou, C.P. Warrens, P.J. Camp, Interactions between Friction Modifiers and Dispersants in Lubricants: The Case of Glycerol Monooleate and Polyisobutylsuccinimide-Polyamine, ACS Applied Materials & Interfaces 11 (2019) 28359-28369.
[42] K. Gholami, S. Jiang, J. Duhamel, Probing the Interactions between Mimics of Pour Point Depressants (PPDs) and Viscosity Index Improvers (VIIs) in Engine Oil Using Fluorescently Labeled PPDs, Macromolecules 52 (2019) 2651-2658.
[43] R. M. Mortier, M. F. Fox, S. T. Orszulik, Chemistry and Technology of Lubricants, 3rd Edition, Springer, 2010.
[44] F. Yang, Y. Zhao, J. Sjöblom, C. Li, K.G. Paso, Polymeric Wax Inhibitors and Pour Point Depressants for Waxy Crude Oils: A Critical Review, Journal of Dispersion Science and Technology 36 (2015) 213-225.
[45] I. Minami, Molecular Science of Lubricant Additives, Applied Sciences 7 (2017) 445.
[46] J. Guegan, M. Southby, H. Spikes, Friction Modifier Additives, Synergies and Antagonisms, Tribology Letters 67 (2019) 83.
[47] J. Qu, H. Luo, M. Chi, C. Ma, P.J. Blau, S. Dai, M.B. Viola, Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive, Tribology International 71 (2014) 88-97.
[48] L. Peña-Parás, Extreme pressure properties of nanolubricants for metal-forming applications, Industrial Lubrication and Tribology 68 (2016) 30-34.
[49] H. Spikes, Friction Modifier Additives, Tribology Letters 60 (2015) 5.
[50] A. Singh, P. Chauhan, T.G. Mamatha, A review on tribological performance of lubricants with nanoparticles additives, Materials Today: Proceedings (2019).
[51] Y. Zhou, J. Qu, Ionic Liquids as Lubricant Additives: A Review, ACS Applied Materials & Interfaces 9 (2017) 3209-3222.
[52] J. Sanes, M.-D. Avilés, N. Saurín, T. Espinosa, F.-J. Carrión, M.-D. Bermúdez, Synergy between graphene and ionic liquid lubricant additives, Tribology International 116 (2017) 371-382.
[53] M.-D. Avilés, N. Saurín, J. Sanes, F.-J. Carrión, M.-D. Bermúdez, Ionanocarbon Lubricants. The Combination of Ionic Liquids and Carbon Nanophases in Tribology, Lubricants 5 (2017) 14.
[54] V. Khare, M.-Q. Pham, N. Kumari, H.-S. Yoon, C.-S. Kim, J.-I.L. Park, S.-H. Ahn, Graphene–Ionic Liquid Based Hybrid Nanomaterials as Novel Lubricant for Low Friction and Wear, ACS Applied Materials & Interfaces 5 (2013) 4063-4075.
[55] S. Shahnazar, S. Bagheri, S.B. Abd Hamid, Enhancing lubricant properties by nanoparticle additives, International Journal of Hydrogen Energy 41 (2016) 3153-3170.
[56] N.G. Demas, E.V. Timofeeva, J.L. Routbort, G.R. Fenske, Tribological effects of BN and MoS_2 nanoparticles added to polyalphaolefin oil in piston skirt/cylinder liner tests, American Society of Mechanical Engineers, Tribology Division, TRIB, 2012, pp. 5-7.
[57] Z. Tang, S. Li, A review of recent developments of friction modifiers for liquid lubricants (2007-present), Current Opinion in Solid State and Materials Science 18 (2014) 119-139.
[58] L. Kong, J. Sun, Y. Bao, Preparation, characterization and tribological mechanism of nanofluids, RSC Advances 7 (2017) 12599-12609.
[59] M. Gulzar, H.H. Masjuki, M.A. Kalam, M. Varman, N.W.M. Zulkifli, R.A. Mufti, R. Zahid, Tribological performance of nanoparticles as lubricating oil additives, Journal of Nanoparticle Research 18 (2016) 223.
[60] I. Khan, K. Saeed, I. Khan, Nanoparticles: Properties, applications and toxicities, Arabian Journal of Chemistry 12 (2019) 908-931.
[61] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, C60: Buckminsterfullerene, Nature 318 (1985) 162-163.
[62] G.-J. Lee, C.K. Rhee, Enhanced thermal conductivity of nanofluids containing graphene nanoplatelets prepared by ultrasound irradiation, Journal of Materials Science 49 (2014) 1506-1511.
[63] H. Kinoshita, Y. Nishina, A.A. Alias, M. Fujii, Tribological properties of monolayer graphene oxide sheets as water-based lubricant additives, Carbon 66 (2014) 720-723.
[64] V. Eswaraiah, V. Sankaranarayanan, S. Ramaprabhu, Graphene-Based Engine Oil Nanofluids for Tribological Applications, ACS Applied Materials & Interfaces 3 (2011) 4221-4227.

[65] D. Zheng, Z.-b. Cai, M.-x. Shen, Z.-y. Li, M.-h. Zhu, Investigation of the tribology behaviour of the graphene nanosheets as oil additives on textured alloy cast iron surface, Applied Surface Science 387 (2016) 66-75.
[66] S.S.N. Azman, N.W.M. Zulkifli, H. Masjuki, M. Gulzar, R. Zahid, Study of tribological properties of lubricating oil blend added with graphene nanoplatelets, Journal of Materials Research 31 (2016) 1932-1938.
[67] M. Sarno, A. Senatore, C. Cirillo, V. Petrone, P. Ciambelli, Oil lubricant tribological behaviour improvement through dispersion of few layer graphene oxide, Journal of Nanoscience and Nanotechnology 14 (2014) 4960-4968.
[68] W. Khalil, A. Mohamed, M. Bayoumi, T.A. Osman, Tribological properties of dispersed carbon nanotubes in lubricant, Fullerenes, Nanotubes and Carbon Nanostructures 24 (2016) 479-485.
[69] J. Lee, S. Cho, Y. Hwang, C. Lee, S.H. Kim, Enhancement of Lubrication Properties of Nano-oil by Controlling the Amount of Fullerene Nanoparticle Additives, Tribology Letters 28 (2007) 203-208.
[70] A. Raina, A. Anand, Lubrication performance of synthetic oil mixed with diamond nanoparticles: Effect of concentration, Materials Today: Proceedings 5 (2018) 20588-20594.
[71] G. Yang, Z. Zhang, S. Zhang, L. Yu, P. Zhang, Synthesis and characterization of highly stable dispersions of copper nanoparticles by a novel one-pot method, Materials Research Bulletin 48 (2013) 1716-1719.
[72] J.L. Viesca, A. Hernández Battez, R. González, R. Chou, J.J. Cabello, Antiwear properties of carbon-coated copper nanoparticles used as an additive to a polyalphaolefin, Tribology International 44 (2011) 829-833.
[73] J. Padgurskas, R. Rukuiza, I. Prosyčevas, R. Kreivaitis, Tribological properties of lubricant additives of Fe, Cu and Co nanoparticles, Tribology International 60 (2013) 224-232.
[74] S.J. Asadauskas, R. Kreivaitis, G. Bikulčius, A. Grigucevičienė, J. Padgurskas, Tribological effects of Cu, Fe and Zn nano-particles, suspended in mineral and bio-based oils, Lubrication Science 28 (2016) 157-176.
[75] M. Flores-Castañeda, E. Camps, M. Camacho-Lopez, S. Muhl, E. García, M. Figueroa, Bismuth nanoparticles synthesized by laser ablation in lubricant oils for tribological tests, Journal of Alloys and Compounds 643 (2014).
[76] Y.Y. Wu, W.C. Tsui, T.C. Liu, Experimental analysis of tribological properties of lubricating oils with nanoparticle additives, Wear 262 (2007) 819-825.
[77] A. Hernández Battez, R. González, J.L. Viesca, J.E. Fernández, J.M. Díaz Fernández, A. Machado, R. Chou, J. Riba, CuO, ZrO_2 and ZnO nanoparticles as antiwear additive in oil lubricants, Wear 265 (2008) 422-428.
[78] S.M. Alves, V.S. Mello, E.A. Faria, A.P.P. Camargo, Nanolubricants developed from tiny CuO nanoparticles, Tribology International 100 (2016) 263-271.
[79] G. Zhou, Y. Zhu, X. Wang, M. Xia, Y. Zhang, H. Ding, Sliding tribological properties of 0.45% carbon steel lubricated with Fe_3O_4 magnetic nano-particle additives in baseoil, Wear 301 (2013) 753-757.
[80] Q. Zhang, B. Wu, R. Song, H. Song, J. Zhang, X. Hu, Preparation, characterization and tribological properties of polyalphaolefin with magnetic reduced graphene oxide/Fe_3O_4, Tribology International 141 (2020) 105952.
[81] T. Luo, X. Wei, X. Huang, L. Huang, F. Yang, Tribological properties of Al_2O_3 nanoparticles as lubricating oil additives, Ceramics International 40 (2014) 7143-7149.
[82] D.X. Peng, Size effects of SiO_2 nanoparticles as oil additives on tribology of lubricant, Industrial Lubrication and Tribology 62 (2010) 111-120.
[83] V. Cortes, K. Sanchez, R. Gonzalez, M. Alcoutlabi, J.A. Ortega, The Performance of SiO_2 and TiO_2 Nanoparticles as Lubricant Additives in Sunflower Oil, Lubricants 8 (2020) 10.
[84] X. Hou, J. He, L. Yu, Z. Li, Z. Zhang, P. Zhang, Preparation and tribological properties of fluorosilane surface-modified lanthanum trifluoride nanoparticles as additive of fluoro silicone oil, Applied Surface Science 316 (2014) 515-523.

[85] L. Pena-Paras, D. Maldonado-Cortes, J. Taha-Tijerina, M. Irigoyen, J. Guerra, Experimental evaluation of the tribological behaviour of CeO_2 nanolubricants under extreme pressures, IOP Conference Series: Materials Science and Engineering 400 (2018) 072003.
[86] S. Kumari, O.P. Sharma, R. Gusain, H.P. Mungse, A. Kukrety, N. Kumar, H. Sugimura, O.P. Khatri, Alkyl-Chain-Grafted Hexagonal Boron Nitride Nanoplatelets as Oil-Dispersible Additives for Friction and Wear Reduction, ACS Applied Materials & Interfaces 7 (2015) 3708-3716.
[87] F.U. Shah, S. Glavatskih, O.N. Antzutkin, Boron in Tribology: From Borates to Ionic Liquids, Tribology Letters 51 (2013) 281-301.
[88] A. Gachechiladze, O. Tsagareishvili, B. Margiev, L. Rukhadze, M. Darchiashvili, L. Chkhartishvili, Nanopowdered h-BN as a wear-reducing eco-friendly material, 2019, pp. 2389-2408.
[89] Y. Wang, Z. Wan, L. Lu, Z. Zhang, Y. Tang, Friction and wear mechanisms of castor oil with addition of hexagonal boron nitride nanoparticles, Tribology International 124 (2018) 10-22.
[90] H. Xie, B. Jiang, J. He, X. Xia, F. Pan, Lubrication performance of MoS_2 and SiO_2 nanoparticles as lubricant additives in magnesium alloy-steel contacts, Tribology International 93 (2016) 63-70.
[91] W. Li, S. Zheng, B. Cao, S. Ma, Friction and wear properties of ZrO_2/SiO_2 composite nanoparticles, Journal of Nanoparticle Research 13 (2011) 2129-2137.
[92] T. Luo, X. Wei, H. Zhao, G. Cai, X. Zheng, Tribology properties of Al_2O_3/TiO_2 nanocomposites as lubricant additives, Ceramics International 40 (2014) 10103-10109.
[93] D.K. Devendiran, V.A. Amirtham, A review on preparation, characterization, properties and applications of nanofluids, Renewable and Sustainable Energy Reviews 60 (2016) 21-40.
[94] Q. Wan, Y. Jin, P. Sun, Y. Ding, Rheological and tribological behaviour of lubricating oils containing platelet MoS_2 nanoparticles, Journal of Nanoparticle Research 16 (2014) 2386.
[95] Z.S. Hu, J.X. Dong, G.X. Chen, J.Z. He, Preparation and tribological properties of nanoparticle lanthanum borate, Wear 243 (2000) 43-47.
[96] H.P. Mungse, O.P. Khatri, Chemically Functionalized Reduced Graphene Oxide as a Novel Material for Reduction of Friction and Wear, The Journal of Physical Chemistry C 118 (2014) 14394-14402.
[97] M.-D. Bermúdez, A.-E. Jiménez, J. Sanes, F.-J. Carrión, Ionic Liquids as Advanced Lubricant Fluids, Molecules 14 (2009) 2888-2908.
[98] A.E. Somers, P.C. Howlett, D.R. MacFarlane, M. Forsyth, A Review of Ionic Liquid Lubricants, Lubricants 1 (2013) 3-21.
[99] A.E. Somers, R. Yunis, M.B. Armand, J.M. Pringle, D.R. MacFarlane, M. Forsyth, Towards Phosphorus Free Ionic Liquid Anti-Wear Lubricant Additives, Lubricants 4 (2016) 22.
[100] J. Qu, D.G. Bansal, B. Yu, J.Y. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, Antiwear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive, ACS Applied Materials & Interfaces 4 (2012) 997-1002.
[101] B. Yu, D.G. Bansal, J. Qu, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, Oil-miscible and non-corrosive phosphonium-based ionic liquids as candidate lubricant additives, Wear 289 (2012) 58-64.
[102] Y. Zhou, J. Dyck, T.W. Graham, H. Luo, D.N. Leonard, J. Qu, Ionic Liquids Composed of Phosphonium Cations and Organophosphate, Carboxylate, and Sulfonate Anions as Lubricant Antiwear Additives, Langmuir 30 (2014) 13301-13311.
[103] W.C. Barnhill, H. Luo, H.M. Meyer, C. Ma, M. Chi, B.L. Papke, J. Qu, Tertiary and Quaternary Ammonium-Phosphate Ionic Liquids as Lubricant Additives, Tribology Letters 63 (2016) 22.
[104] S. Yang, J.S.S. Wong, F. Zhou, Ionic Liquid Additives for Mixed and Elastohydrodynamic Lubrication, Tribology Transactions 61 (2018) 816-826.
[105] A.S. A. S, E. Rahim, N. Talib, K. Kamdani, M. Rahim, S. Samion, Performance Evaluation of Palm-Olein TMP Ester Containing Hexagonal Boron Nitride and an Oil Miscible Ionic Liquid as Bio-Based Metalworking Fluids, Journal of Mechanical Engineering SI 4 (2017) 223-234.

[106] Y. Li, S. Zhang, Q. Ding, H. Li, B. Qin, L. Hu, Understanding the synergistic lubrication effect of 2-mercaptobenzothiazolate based ionic liquids and Mo nanoparticles as hybrid additives, Tribology International 125 (2018) 39-45.
[107] A. Senatore, M. Pisaturo, D. Guida, Polyalkylene Glycol Based Lubricants and Tribological Behaviour: Role of Ionic Liquids and Graphene Oxide as Additives, Journal of Nanoscience and Nanotechnology 18 (2018) 913-924.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

2. MATERIALS AND METHODS

The general diagram of the methodology followed in this work is showed in figure 2.1. In the next sections, each step and the corresponding equipment are described.

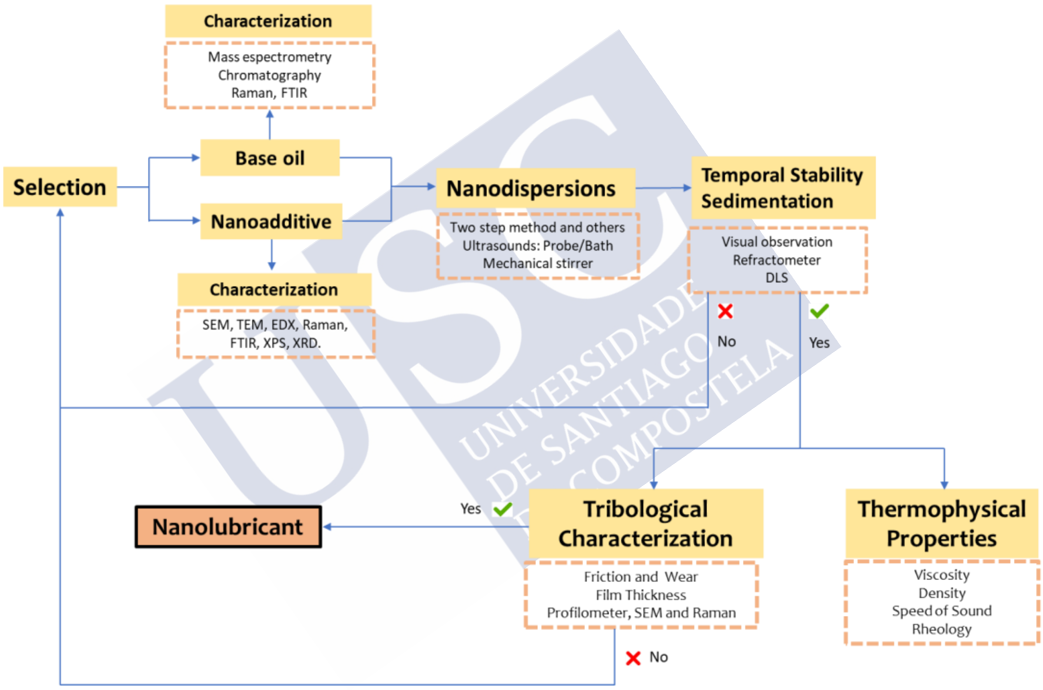


Figure 2.1 Diagram of the experimental procedure.

2.1. SELECTION OF BASE OILS AND NANOPARTICLES

In this PhD Thesis several base oils and formulated lubricants were initially selected in collaboration with Repsol, Croda, Verkol and Enel Green Power companies. As regards nanoparticles, we have initially chosen several metal oxides, hexagonal boron nitride (h-BN), graphene oxide (GO) and graphene nanoplatelets (GnPs). For this initial selection we have considered the commercial availability, the cost and the tribological behavior reported in the literature. It should be taken into account that most of the published articles of nanolubricants did not report their stability. Firstly, temporal stability and preliminary tribological tests were performed with nanodispersions composed by different combinations of nanoparticles and base oils. Tables 2.1 and 2.2 summarize the stability studies through visual observation of all nanodispersions prepared along the entire Thesis. The obtained results in both tests for the initial nanoparticle/base oil combinations were not always satisfactory. Therefore, new strategies were carried out, as synthesis of new nanoparticles and use of dispersants or ionic liquid as well as new methods to prepare the nanodispersions to improve the stability and tribological behavior. These strategies are described in detail in section 2.4. The ionic liquid mentioned in Table 2.1 is tri(butyl) ethylphosphonium diethylphosphate, which was chosen for the good tribological and stability results as additive of same ester base oil obtained in a previous PhD Thesis of our laboratory [1]. The analyzed mass concentrations range from 0 to 1 wt%, depending on the nanoadditive type.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Table 2.1 Studied combinations of base oils with nanoparticles.

Oil	Nanoparticle	Source	Visual Stability Time
Trimethylolpropane trioleate, TMPTO (Croda)	Hexagonal Boron Nitride (h-BN)	Iolitec	48 hours
	Graphene Nanoplatelets (GnP)	Iolitec	96 hours
	Niquel Oxide (NiO)	Iolitec	< 24 h
	Ferrous Oxide (FeO)	Iolitec	< 24 h
	Magnesium Oxide (MgO)	Iolitec	< 24 h
	Graphene Oxide (GO)	Nanoinnova	< 12 h
	Reduced Graphene Oxide (rGO)	Synthesized	148 hours
	Magnetite (Fe_3O_4) 6.3 nm	Synthesized	> 11 months
	Magnetite (Fe_3O_4) 10 nm	Synthesized	> 11 months
	Nd alloy 19 nm	Synthesized	> 11 months
Polyalphaolefin base oil, PAO40 (Repsol)	Hexagonal Boron Nitride (h-BN)	Iolitec	48 hours
	Graphene Nanoplatelets (GnP)	Iolitec	96 hours
	Graphene Oxide (GO)	Nanoinnova	< 24 h
	Reduced Graphene Oxide (rGO)	Synthesized	148 hours
Triisotridecyltrimellitate, TTM (Verkol)	Hexagonal Boron Nitride (h-BN)	Iolitec	48 hours
	Graphene Nanoplatelets (GnP)	Iolitec	96 hours
	IL+ Graphene Nanoplatelets (GnP)	Iolitec	3 weeks
	IL+ Boron Nitride (BN)	Iolitec	3 weeks
	Mica	USC	48 hours
	Kaolin	USC	48 hours
Priolube 1973 Ester (Croda)	Hexagonal Boron Nitride (h-BN)	Iolitec	< 24h
	Graphene Nanoplatelets (GnP)	Iolitec	< 24h
	Niquel Oxide (NiO)	Iolitec	< 12 h
	Ferrous Oxide (FeO)	Iolitec	< 12 h
	Magnesium Oxide (MgO)	Iolitec	< 12 h
	Graphene Oxide (GO)	Nanoinnova	< 12 h

Table 2.1 (continued)

Priolube 1936 Ester (Croda)	Hexagonal Boron Nitride (h-BN)	Iolitec	48 hours
	Graphene Nanoplatelets (GnP)	Iolitec	48 hours
	Niquel Oxide (NiO)	Iolitec	< 24 h
	Ferrous Oxide (FeO)	Iolitec	< 24 h
	Magnesium Oxide (MgO)	Iolitec	< 24 h
	Graphene Oxide (GO)	Nanoinnova	< 12 h
Dipentaerythritol hexapentanoateDiPEC5 (Croda)	Hexagonal Boron Nitride (h-BN)	Iolitec	< 48 h
Dipentaerythritol hexaheptanoate, DiPEC7 (Croda)	Hexagonal Boron Nitride (h-BN)	Iolitec	< 48 h
G-I (Repsol)	Graphene Oxide (GO)	Nanoinnova	< 24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	24 hours
G-III (Repsol)	Graphene Oxide (GO)	Nanoinnova	< 24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	24 hours

Table 2.2 Studied combinations of formulated lubricants with nanoparticles.

Lubricant	Nanoparticle	Source	Visual Stability Time
Castrol Tribol 1510, PAO32, Gearbox	Hexagonal Boron Nitride (h-BN)	Iolitec	24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	48 hours
Castrol Optigear X320, PAO32, Gearbox oil	Hexagonal Boron Nitride (h-BN)	Iolitec	24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	24 hours
Klüber GEM4-3200, PAO32, Gearbox oil	Hexagonal Boron Nitride (h-BN)	Iolitec	24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	24 hours
Mobil 32 Excel, Synthetic, Brakes oil	Hexagonal Boron Nitride (h-BN)	Iolitec	24 hours
	Graphene Nanoplatelets (GnP	Iolitec	24 hours
Exxonmobil SHC 524, Synthetic, Hydraulic oil	Hexagonal Boron Nitride (h-BN)	Iolitec	24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	24 hours
Repsol Telex E32, Mineral, Hydraulic oil	Hexagonal Boron Nitride (h-BN)	Iolitec	24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	24 hours
	Graphene Oxide (GO)	Nanoinnova	< 24 hours
Diesel Engine Oil, Mineral, 15W40	Hexagonal Boron Nitride (h-BN)	Iolitec	24 hours
	Graphene Nanoplatelets (GnP)	Iolitec	24 hours
	Graphene Oxide (GO)	Nanoinnova	< 24 hours

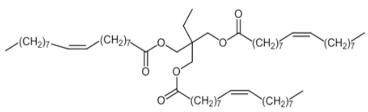
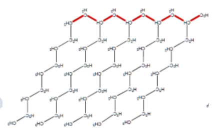
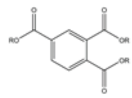
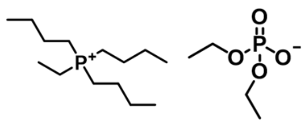
The selected base oils (Table 2.1) are four different esters: trimethylolpropane trioleate (TMPTO), triisotridecyl trimellitate (TTM), Priolube 1936 and Priolube 1973 which are

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

classified in the group V of the American Petroleum Institute (API) and a synthetic polyalphaolefin (PAO40) which belongs to the group IV of API classification, as well as two mineral oils: G-I and G-III (Type I and III, respectively). These oils were supplied by the partners (Croda, Repsol and Verkol) supporting the two national research projects. The chosen commercial lubricants (Table 2.2) were formulated by Repsol, Exxonmobil, Klüber and Castrol for gearboxes, brakes and hydraulic system of wind turbines, and for engines.

As regards nanoparticles apart from the initial selection of oxides, h-BN and GnPs, the initial stability and tribological tests (more details are given in sections 2.4 and 3.9) lead us to synthetize the following nanomaterials: reduced graphene oxide (rGO) and three superparamagnetic nanoparticles coated with oleic acid (Fe_3O_4-OA of two sizes, 6.3 and 10 nm and a Nd alloy-OA, 19 nm). In addition, some stability tests were carried out with two different types of surfactants (Span 80 and sodium dodecyl sulfate). As already indicated, the use as additive of the ionic liquid tri(butyl) ethylphosphonium diethylphosphate was also tested to improve both stability and tribological behavior. As a result of the development of this strategy, the oils and nanoparticles indicated in Table 2.3 and 2.4 were selected in this PhD Thesis for deeper studies. Current lubricants used for gears of wind turbines among others applications are composed by PAOs and esters. The later are used because current additives are more soluble in esters than in PAOs. In the case of the wind turbine gearbox lubricants, usually a mixture PAO32, PAO40 and an ester is used as base oil. For these reason PAO40 and two esters (TMPTO and TTM) of different viscosity were chosen. PAO40 is a high viscosity PAO, which is mainly used as high-performance functional base fluid in several industrial and automotive applications as gear oil, compressor oil, hydraulic fluid, grease and engine oil [2]. TMPTO is a non-fully saturated ester synthetized from the oleic fatty acid and trimethylolpropane. This base oil was chosen because of the following properties: high viscosity index (VI = 190), high biodegradability (even higher than 90% in ecological environments), nonflammability, excellent lubricating properties [3,4]. It is considered as a biolubricant [3].The study of biodegradable and efficient lubricants as substitutes of mineral oils is encouraged for environmental issues and energy savings. In addition, TMPTO has better oxidative stability and better low-temperature properties than other possible substitutes such as vegetable oils [3]. TMPTO is extensively used as hydraulic oil, chain oil and metallurgy fluid. In addition, due to its environmentally friendly nature, this oil is a promising alternative to mineral oils and polyalphaolefins (PAOs), not only for these applications but also in marine and agricultural environments [5,6]. On the other hand, the trimellitate ester TTM was selected by its high viscosity, close to the viscoity grade of the gear oils of wind turbines. The main advantages of trimellitates are low volatility, good thermal stability, good stability to oxidation, high film strength, good low temperature properties, high flashpoints and good hydrolytic stability. Trimellitate esters are used as specialty lubricants including compressor fluids, two stroke oils, greases or chain oils [2].

Table 2.3 Properties of base lubricants and ionic liquid studied in this PhD Thesis: ν, kinematic viscosity and VI, viscosity index.

Base Oil/Ionic Liquid	*Source*	ν (313.15 K)[a] mm^2/s	*VI*[a]	*Chemical structure*
		Base Oils		
Trimethylolpropane trioleate (TMPTO)	Croda	50.1	190	
PAO40	Repsol	402.1	129	
Triisotridecyl trimellitate (TTM)	Verkol	321.2	74	
		Ionic Liquid		
Tri(butyl) ethylphosphonium diethylphosphate	Cytec	225	82	

[a]Measured by an Anton Paar Stabinger SVM3000 device.

Table 2.4 Characteristics of the nanoadditives used in this PhD Thesis.

Nanoparticle	*Source*	*Mole Fraction Purity*[a]	*Average size* / nm
h-BN	Iolitec	0.99	70
GnP	Iolitec	0.995	11-15[b]
rGO	Synthesized	-	0.7-1.2[b]
Fe_3O_4-OA	Synthesized	-	6.3
Fe_3O_4-OA	Synthesized	-	10
Nd alloy-OA	Synthesized	-	19

[a]Determined by the supplier
[b] Thickness

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Graphene nanoplatelets (lot NCP068011 and CAS number 1034343-98-0), have a mole fraction purity of 0.995, a medium size of (11–15) nm and a bulk density of 2.25 g cm^{-3}, while h-BN nanoparticles (lot MNC018001 and CAS Number: 10043-11-5) present a mole fraction purity of 0.99, a nominal diameter of 70 nm, a specific average area of 19.4 m^2/g and a bulk density of 2.29 g cm^{-3}. Both nanoadditives were supplied by Iolitec, GmbH, Germany. The synthesis of rGO and the procedure followed with coated superparamagnetic nanoparticles are detailed in section 2.4

2.2. CHARACTERIZATION TECHNIQUES

In this section the techniques (Fourier-transform infrared spectroscopy, Raman spectroscopy, high phase liquid chromatography coupled with mass spectrometry, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy, among others) used to characterize the base oils, nanoparticles and nanolubricants are presented. These analyses were performed in collaboration with the Network of Infrastructures to Support Research and Technological Development (RIAIDT) of the University of Santiago de Compostela and with the Nanomagnetism and Nanotechnology Group (NanoMag) of the University of Santiago de Compostela as well as with the Center for Scientific-Technological Research Support (C.A.C.T.I.) of the University of Vigo.

Fourier-transform infrared spectroscopy

This non-destructive chemical characterization technique is one of the most powerful tools for identifying chemical bonds (functional groups) of compounds. Characteristic peaks of oils and nanoparticles were identified by Fourier-transform infrared spectroscopy. For this aim, a FTIR VARIAN 670-IR (Figure 2.2) spectrometer coupled with a microscope 610 IR mapping was used configured to work in the medium and far infrared region. This apparatus is also equipped with an Attenuated Total Reflection (ATR) accessory, ATR PIKE that allows measuring the absorbance spectra of nanoparticles and oils. In addition, this apparatus was also used to study the possible chemical bonds formation of nanolubricants between nanoparticles and the base oils.

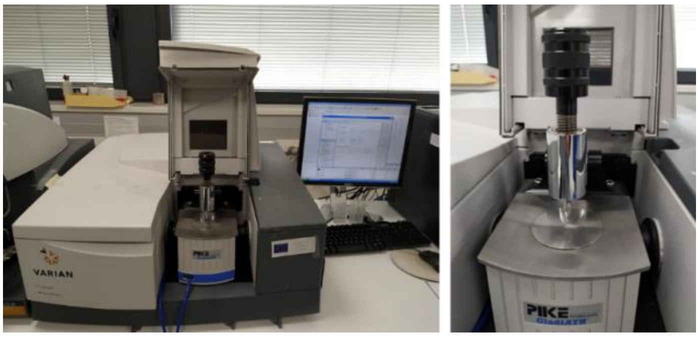


Figure 2.2 Fourier transform infrared FTIR VARIAN 670-IR spectrometer (RIAIDT of the University of Santiago de Compostela).

Raman spectroscopy

This technique is one of the most used during this PhD Thesis, since it has been employed to determine the number of layers in graphene nanoplatelets, to analyze the oxygen content of both graphene oxide and reduced graphene oxide and also to determine characteristic bands of h-BN in the visible range, among others. These Raman measurements were performed with a Renishaw confocal microscope model InVia Reflex using an argon ion laser. This apparatus (Figure 2.3) is equipped with a confocal LEICA DM microscope, a motorized platform XYZ for Raman mapping and a variable spot laser from 1 to 300 μm depending on the objective and the employed wavelength. On the other hand, elemental mapping and Raman spectroscopy were also used to characterize the film on the wear track, in order to know the role that nanoparticles or ionic liquid plays in the reduction of wear. For this purpose, a WITec alpha300R+ confocal Raman microscope (Figure 2.4) was used, which can operate at three different wavelengths (488, 532 and 785 nm). This device has two scanning systems, a coarse motorized stage for large areas and a piezo stage for subnanometer adjustments. It can provide both 3D optical and chemical information.

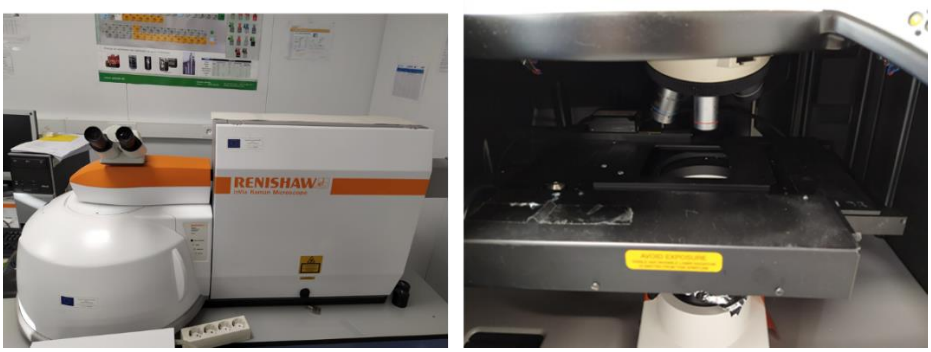


Figure 2.3 "InVia Reflex" Renishaw confocal Raman microscope (RIAIDT of the University of Santiago de Compostela).

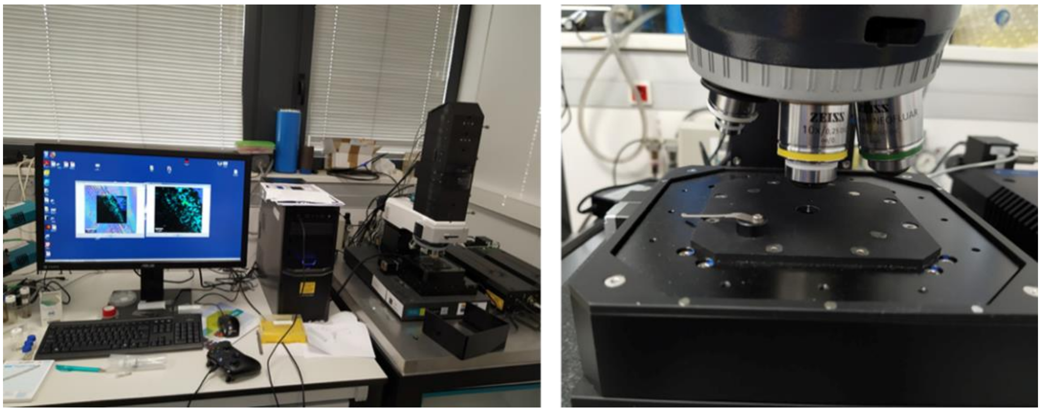


Figure 2.4 WITec alpha300R+ confocal Raman microscope (RIAIDT of the University of Santiago de Compostela).

Scanning electron microscopy

This technique was employed to obtain the morphology of nanoparticles and to observe the wear tracks produced in steel samples after the tribological tests. For this aim, a scanning electron microscope Zeiss FESEM Ultra Plus (SEM) (Figure 2.5) was used. This device works with an acceleration voltage range from 0.02 to 30 kV and resolutions: 1.0 nm/15 kV, 1.7 nm/ 1 kV, 4.0 nm/0.1 kV. This apparatus is equipped with a detector for energy dispersive X-ray microanalysis (EDX) which allows to obtain chemical elements distributions and atomic compositions. In order to obtain the SEM images of nanoparticles, they are placed on active carbon films supported by a carriage with multiple positions.

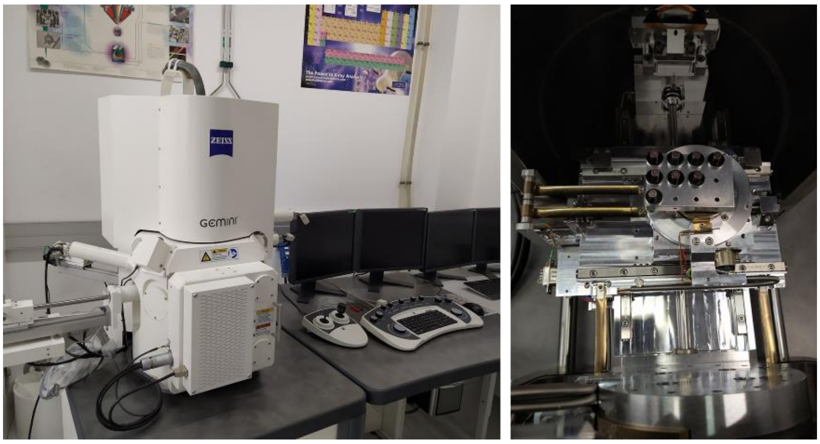


Figure 2.5 a) Zeiss FESEM Ultra Plus Scanning Electron Microscope and b) carriage of samples support. (RIAIDT of the University of Santiago de Compostela).

Transmission electron microscopy

In order to analyze the size and shape of nanoparticles and aggregates a JEOL JEM-2010 and a JEOL JEM-1011 high resolution transmission electron microscope (TEM) were utilized (Figure 2.6 and 2.7). The first one is configured with a high brightness lanthanum hexaboride (LaB_6) source and can operate between 80 and 200 kV accelerating voltage. As regards JEOL JEM-1011, it has a wolfram filament and works at an acceleration voltage between 40 and 100 kV. Nanopowders were dispersed in a volatile organic solvent (1-butanol or 2-propanol) before the analysis and placed in copper grids with a carbon film. This technique cannot be used to study the aggregation of the nanoparticles in the base oil since as works at high vacuum, a volatile solvent is needed.

Figure 2.6 JEOL JEM-2010 Transmission Electron Microscope (RIAIDT of the University of Santiago de Compostela).

Figure 2.7 JEOL JEM-1011 Transmission Electron Microscope (RIAIDT of the University of Santiago de Compostela).

X-Ray photoelectron spectroscopy (XPS)

X-Ray photoelectron spectroscopy permits, among others applications, to obtain quantitative results (C/O atomic ratio, elemental composition and functional groups bands) of graphene oxide (GO) and reduced graphene oxide (rGO). For this task, a Thermo Scientific K-Alpha ESCA instrument equipped with aluminium Kα monochromatized radiation at 1486.6 eV X-ray source was utilized (Figure 2.8). Due to the non-conductive nature of samples it is necessary to use an electron flood gun to minimize surface charging. Neutralization of the surface charge was performed by using both a low energy flood gun (electrons in the range 0 to 14 eV) and a low energy Argon ions gun. Photoelectrons were collected from a take-off angle of 90º relative to the sample surface. The measurements were done in a constant analyzer energy mode (CAE) with a 100 eV pass energy for survey spectra and 20 eV pass energy for high resolution spectra.

Figure 2.8 Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) (C.A.C.T.I. of the University of Vigo).

HPLC coupled to Mass spectrometry

High-performance liquid chromatography (HPLC) coupled to a quadrupole orthogonal acceleration time-of-flight mass spectrometer was used to know the chemical composition and molecular mass of the TMPTO base oil. For this task, a Bruker micrOTOFQ™ (Figure 2.9) equipped with an electrospray ionization source (ESI) was employed. This apparatus operates in a mass range of 20-20000 m/z and with a resolution of 15000 (FWHM).

Figure 2.9 Bruker micrOTOFQ HPLC coupled to a quadrupole orthogonal mass spectrometer (RIAIDT of the University of Santiago de Compostela).

X ray powder diffraction (XRPD)

X ray powder diffraction is the technique used to analyze the structural characterization of magnetic nanoparticles. A Philips PW1710 diffractometer, Figure 2.10, (Cu Kα radiation source, λ= 1.54186 Å) equipped with a graphite monochromator was employed. The measurement conditions were: 40 kV, 30 mA, angular measurement range 10º ≤ 2θ ≤ 80º, step size of 0.02º and counting time of 2 s per step.

Figure 2.10 Philips PW1710 diffractometer (RIAIDT of the University of Santiago de Compostela).

Thermogravimetric analysis (TGA)

This is a common technique for measuring the weight change of a material as a function of temperature. In this case, it was used to estimate the oleic acid content in the synthesized magnetic nanoparticles as well as the number of oleic acid molecules per surface area of each nanoparticle. For this purpose, a Perkin Elmer Pirys 7 TGA was used heating from 50 to 850 ºC at 10ºC/min under a nitrogen flow of 20 mL/min.

Figure 2.11 Perkin Elmer Pirys 7 TGA (NanoMag, University of Santiago de Compostela).

Magnetization

Hysteresis cycles of magnetic nanoparticles were measured with a vibrating sample magnetometer (VSM) DMS-1660 (Figure 2.12) that belongs to the Nanomagnetism and Nanotechnology Group (NanoMag) of the University of Santiago de Compostela. For this purpose, a magnetic field was applied, whose values vary according to the sequence:10 kOe → 0 Oe → -10 kOe → 0 Oe → 10 kOe. The data were recorded at 100 Oe intervals, between 0 and 4000 Oe, while between 4000 and 10000 Oe were collected at 500 Oe intervals.

Figure 2.12 Vibrating sample magnetometer (VSM) DMS-1660 (NanoMag, University of Santiago de Compostela).

2.3. PREPARATION OF NANODISPERSIONS

The preparation of nanofluids is one of the keys to achieve good stability against sedimentation. For this reason, an appropriate methodology should be used with an optimum concentration for the use of nanolubricants in industrial applications. Usually two methods are used to prepare nanofluids: single-step method and two-step method [7-10]. In the first one the production of nanoparticles and their dispersion in liquids occur at the same time [11], being vapor deposition the method most commonly used [9]. Generally, with this method good stability results are achieved as well as a low agglomeration of the nanoparticles, although it is expensive [10]. On the other hand, the two-step method (Figure 2.13) consists on a) the nanopowders are incorporated in the oil b) the resulting system is homogenized, usually through ultrasonication. The two-step method is the most widely utilized to prepare nanofluids due to it is the most economical [10].

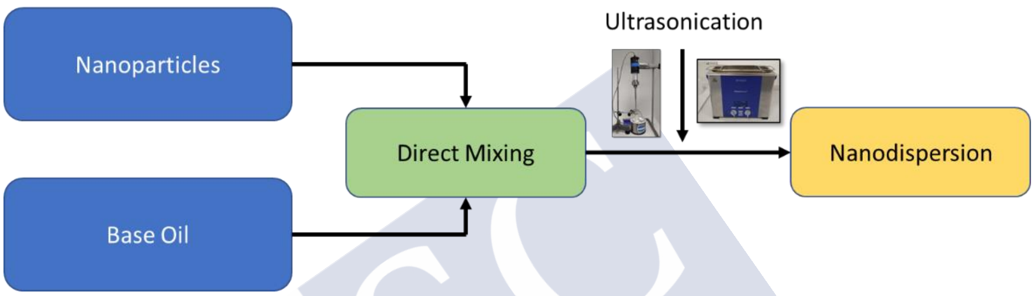


Figure 2.13 Preparation process of nanodispersions by two-step method using ultrasonic probe or bath.

In this PhD Thesis the two-step method was employed to prepare nanodispersions with GnP, h-BN, GO or rGO nanoparticles. Using a Sartorius MC 210P microbalance (precision of 0.00001 g), Figure 2.14a, the mass concentration of nanoparticles in the oil was determined. As regards nanodispersion homogenization, two devices were used: an ultrasonic probe (HD 2200 Sonopuls, Figure 2.14c), and an ultrasonic bath (FB11203 Fisherbrand, Figure 2.14b). The ultrasounds tip conduces the acoustic energy from the transducer into the nanodispersion, this energy depends on different parameters such as effective power, the sonication time and the diameter and shape of the ultrasounds tip [12]. The preparation conditions are an effective power of 200 W, amplitude of 302 μm, a shape and diameter tip of MS73 and 3 mm, and a sonication time of one hour. It should be mentioned that in order to avoid the samples overheating during the sonication process, they were cooled using an ice-water bath. This method was used for h-BN nanodispersions based on TMPTO. As regards carbon-based nanoparticles usually ultrasonic bath is preferred [12,13]. For this type of homogenization, the sonication time was 4 h working in continuous mode, and an effective power of 180 W at a 37 kHz frequency was used.

Figure 2.14 Different devices for nanolubricants preparation: a) High precision Sartorius MC 210P microbalance, b) Fisherbrand ultrasonic bath FB11203 and c) ultrasonic HD 2200 Sonopuls probe.

As regards nanodispersions containing the ionic liquid, the preparation of samples was a bit different in comparison to the aforementioned two-step method [14]. First, nanopowders (h-BN or GnPs) were added to the IL. Then, this ensemble was placed in an agate mortar and mechanically mixed for 5 min and afterwards mixed with the base oil (TTM). Finally, the nanodispersions were sonicated for 4 h by ultrasounds bath, operating under the same conditions described previously.

In the case of superparamagnetic nanodispersions (Fe_3O_4 and Nd alloy) based on TMPTO base oil, the procedure carried out was different (Figure 2.15). Nanoparticles which were suspended in cyclohexane after the synthesis were transferred to another high volatile solvent. The nanoparticles concentration was determined by thermogravimetry and the high volatile solvent dispersion was added to the base oil and mixed by ultrasonic agitation combining bath and probe for a total time of 15 minutes. Then, the solvent was removed from the sample by boiling with a rotary evaporator resulting of this step the magnetic nanolubricants. Finally, these nanolubricants were sonicated in the ultrasonic bath for 4 hours.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

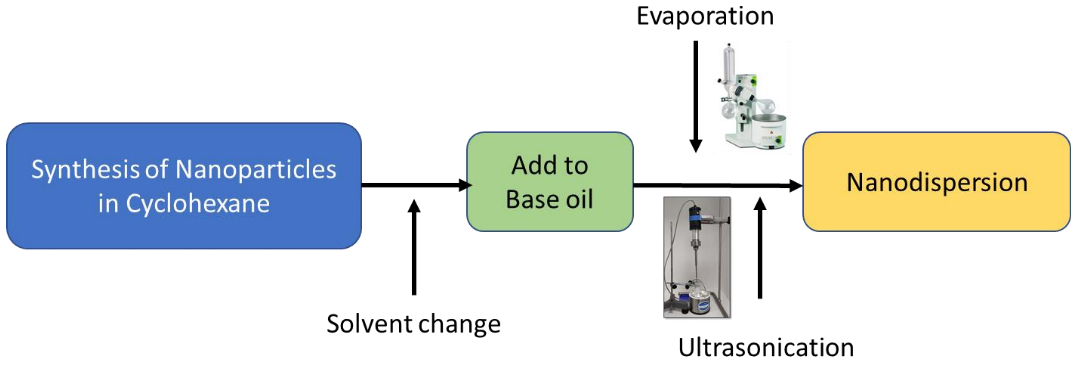


Figure 2.15 Preparation process of magnetic nanodispersions by a modified two-step method.

2.4. Nanodispersions Stability

One of the biggest challenges concerning nanolubricants is to achieve a good stability of the nanoparticles against sedimentation. Nanoparticles in the base oil should show long-term stability in order to perform effectively as lubricant additives since otherwise the properties of the nanolubricants would vary limiting their use in the industry. In the literature there are numerous articles about the stability of nanoparticles in fluids, the methods to evaluate their stability and also the stability enhancement processes, although most of them concern thermal fluids [15,16]. Specifically, aggregation and sedimentation of nanoparticles are considered the two more important aspects affecting nanofluid stability [16]. Some factors as the nanoparticle's properties (particle type, size, shape or coating), the base oil properties (density, viscosity or chemical structure), the nanoparticle concentration, the preparation method or the use of dispersants influence the stability of nanolubricants. Sedimentation is the process through nanoparticles settling down at the bottom of the base fluid. Sedimentation rate, υ_0, can be estimated for most of spherical nanoparticles by the Stokes law (Equation 1)

$$\upsilon_0 = \frac{2gr^2(\rho_{np}-\rho)}{9\eta} \qquad (1)$$

where r is the radius of nanoparticle, ρ_{np} is the density of nanoparticle, ρ is the density of base oil and η is its viscosity Thus, the sedimentation rate will be greater the larger the nanoparticle size, the higher the difference between the density of the nanoparticle and the base oil and the lower the oil viscosity.

2.4.1. Possible ways to enhance the nanodispersions stability

Stability of nanofluids can be achieved by electrostatic and steric stabilization. In the first mechanism the aggregation of nanoparticles is inhibited due to the presence of a double layer of electric charges surrounding the nanoparticles. The repulsive forces between particles should be stronger than the attractive forces (van der Waals) in order to avoid the aggregation of nanoparticles [17]. On the other hand, steric stabilization is the procedure in which the nanoparticles are covered by surfactants or by chemical coatings that separate the nanoparticles [18].

Use of surfactants is the simplest way to avoid aggregation of nanoparticles. The surfactants can operate through an electrostatic mechanism (anionic or cationic) or by a steric mechanism, in which they form a micelle-like structure. It should be considered that surfactants change the lubricant properties, such as viscosity, as well as the antifriction and antiwear capability. In this PhD Thesis some stability tests have been carried out with two surfactants (Span 80 and sodium dodecyl sulfate) but, as no improvements in time stability were found, its use was discarded. Nevertheless, as ILs are considered excellent dispersants for the stabilization of well-characterized nanomaterials [19], these compounds were also analyzed as hybrid lubricant additives in combination with nanoparticles.

Chemical modification (also known as coatings) of nanoparticles is another important strategy to stabilize the nanoparticles within the base oil. Generally, organic compounds with polar groups and long hydrocarbon chains are used as modifying agents. These surface modifications allow inorganic nanoparticles to have good solubilities in organic solvents, as base oils [20]. For this reason, in this PhD Thesis coated superparamagnetic nanoparticles synthesized and characterized by NanoMag group, were employed. Furthermore, in the literature it was found that removing oxygen content of GO a better stability of nanolubricants was achieved [21]. Thus, in this PhD Thesis reduced graphene oxide (rGO) nanopowders were selected and synthetized by thermal reduction of GO.

2.4.2. Evaluation of Nanofluids Dispersion Stability

Literature [8,22,23] reports numerous techniques to evaluate the stability of nanodispersions and colloidal suspensions as sediment photograph capturing, UV–Vis spectrophotometry, turbidimetry, dynamic light scattering (DLS) and refractometry.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Nevertheless, Guimarey *et al.* [24] have found that for several nanolubricants, at the concentrations suitable for efficient lubrication, dispersions are too opaque, so the UV-Vis absorbance and the turbidity cannot be analyzed. For this reason, in this PhD Thesis the sediment photograph capturing, DLS and refractometry techniques were used.

Sediment photograph capturing: This method is based on taking pictures of the dispersions every period. It is the most widely used, especially to have a qualitative idea of the stability of nanolubricants. During this PhD Thesis photos of the dispersions were taken every 24 hours, the first one just after the sonication process was finished. For this task the nanodispersions are left at room temperature and without any alteration. In Figure 2.16 it can be seen the set-up used to take the photos.

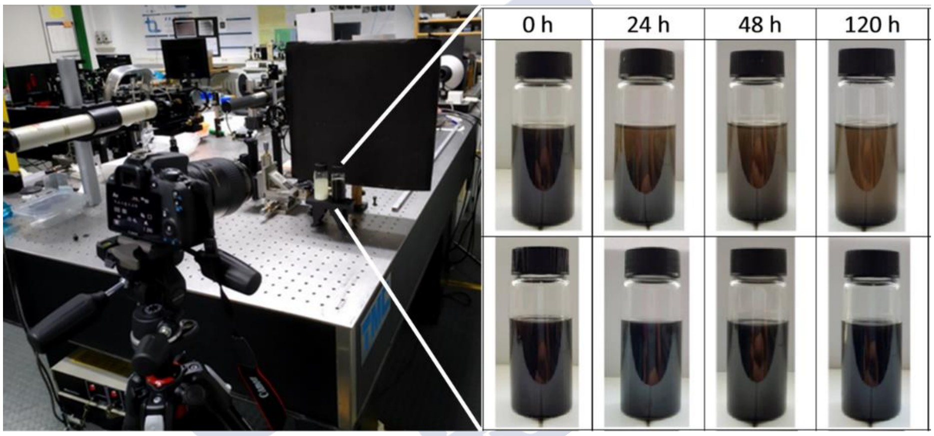


Figure 2.16 Set-up used in the sediment photograph capturing method [25] and images for TMPTO+ (GO and rGO) nanodispersions.

Dynamic light scattering (DLS): This technique was used to measure the nanoparticle size distribution and the average size of aggregates in the lubricant. For this aim, a Malvern Zetasizer Nano ZS analyzer (Figure 2.17) was utilized. The stability of nanodispersions is given by the evolution of the average particle size, in case it increases over time agglomeration occurs while if it decreases sedimentation takes place. In the case that the average particle size remains constant, the nanolubricant is stable. This device is a new high-performance molecular size analyzer that can be used over a large concentration range, although it presents some limitations for opaque samples. These experiments were carried out in CIQUS (Center for Research in Biological Chemistry and Molecular Materials of the

University of Santiago de Compostela) and in the Applied Physics Department of the University of Vigo, during a research stay.

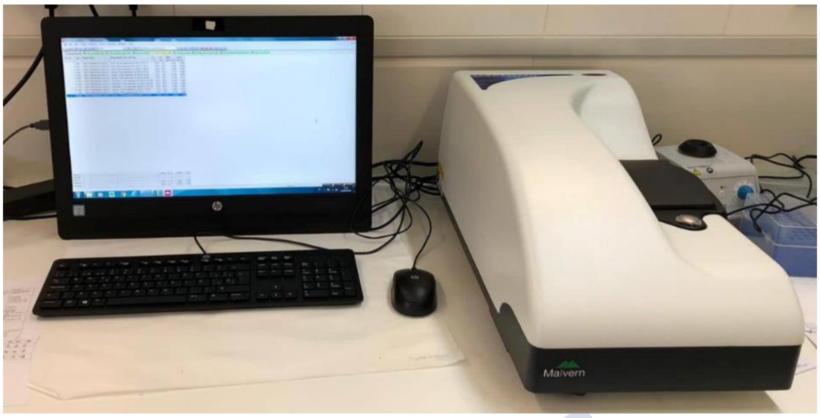


Figure 2.17 Malvern Zetasizer Nano ZS analyzer.

Evolution of refractive index: During this PhD Thesis, a method developed in our group [12,24], was used to analyze the stability of nanodispersions. This method is based on measuring the refractive index of the nanodispersion during time. This one is considered stable when the refractive index hardly varies over time. For this task, a Mettler Toledo refractometer model RA-510M (Figure 2.18a) was used, which can operate at temperatures between 288.15 K and 313.15 K. The measuring cell is an inverted cone-shaped cavity, with stainless steel walls (Figure 2.18b). The base of this cone is a polished surface of a sapphire prism, on which the sample is placed. For the measurement of refractive index, 0.3 mL of sample is needed.

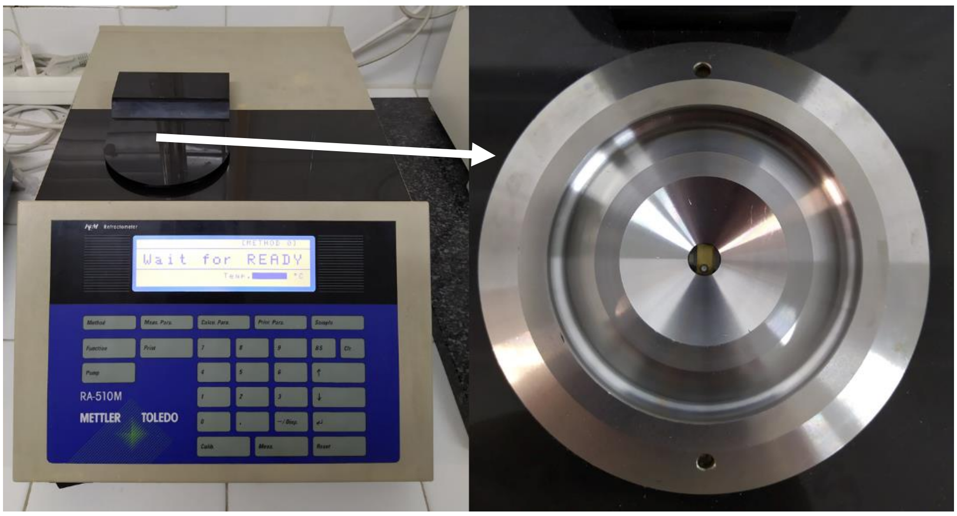


Figure 2.18 a) Mettler Toledo refractometer and b) measuring cell of the refractive index.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

2.5. THERMOPHYSICAL CHARACTERIZATION

This section describes the equipment used to carry out the thermophysical measurements at atmospheric pressure of both the base oils and the prepared nanodispersions. These properties include: density, kinematic and dynamic viscosity, viscosity index and speed of sound, as well as rheological behavior.

2.5.1 Anton Paar Stabinger SVM 3000 viscometer

A rotational viscometer Anton Paar Stabinger SVM 3000 (Figure 2.19a) was used to measure the viscosity, the density and the viscosity index of nanodispersions and base oils. This apparatus has one cell for measuring density and another one to measure the viscosity. Both properties can be measured at atmospheric pressure in the temperature range from 233.15 K to 378.15 K and in a viscosity range from 0.2 mPa·s to 20 Pa·s. Stabinger viscometer has a rapidly rotating outer tube and an inner measuring bob that rotates more slowly (Figure 2.19b) and its operation is based on a modified Couette principle [26]. The density cell is a U-shaped oscillating glass tube, which is excited to produce mechanical resonant vibrations. Density and viscosity cells are filled at the same time, and therefore the measurements are performed simultaneously. The cell temperature is monitored by an integrated thermostat with Peltier cascading elements and is measured with a Pt100 thermometer with an expanded uncertainty ($k = 2$) of 0.02 K from 288.15 to 378.15 K and of 0.05 K outside this range. Expanded experimental uncertainties ($k = 2$) of 1% and 0.0005 g cm^{-3} were estimated for dynamic viscosity and density, respectively. Anton Paar Stabinger viscometer determines, according to ASTM D2270/ISO 2909, the viscosity index of lubricants. This is a dimensionless number which characterize the variation of viscosity when the temperature changes. This parameter is very important for lubricants because during the machinery operation, temperature changes occur, therefore, it is necessary to know how the viscosity of the lubricant varies with the temperature to guarantee a correct operation.

Figure 2.19 Anton Paar Stabinger SV3000 visco-densimeter: a) device and b) operation scheme of viscosity measuring system.

All measurements were performed automatically, in a temperature range of 278.15 to 373.15 K every 5 K. For each measurement 4 mL of sample are needed, which must be introduced without bubbles to avoid an error in the measurement. After the measurement of each sample, it is important to clean the cells properly. For this task, different solvents are introduced in the same way that lubricants. First, petroleum ether is used, then acetone and finally hexane, drying with the air pump of the apparatus. This cleaning is done several times until the air density value reaches the air standard value.

2.5.2. Anton Paar DSA 5000 densimeter

A vibrating tube densimeter, Anton Paar DSA 5000 (Figure 2.20a) was used in order to measure the density and sound speed of nanolubricants and base oils. (Figure 2.20b). Therefore, we can compare the density measurements made with the Anton Paar Stabinger SVM 3000 viscometer, in order to achieve more consistent measurements. DSA 5000 device can measure density and speed of sound at atmospheric pressure between 283.15 K and 338.15 K. With this apparatus the maximum standard uncertainty of density measurements (for samples with viscosity higher than 100 mPa·s) is 0.0002 g·cm^{-3} and for samples with a viscosity lower than 30 mPa·s is 0.00004 g·cm^{-3}. The speed of sound was also measured at an operating frequency of 3 MHz, with a standard uncertainty of 2 m·s^{-1}. The cleaning of this equipment is carried out in the same way as Anton Paar Stabinger SVM 3000, until reaching the reference value of air density.

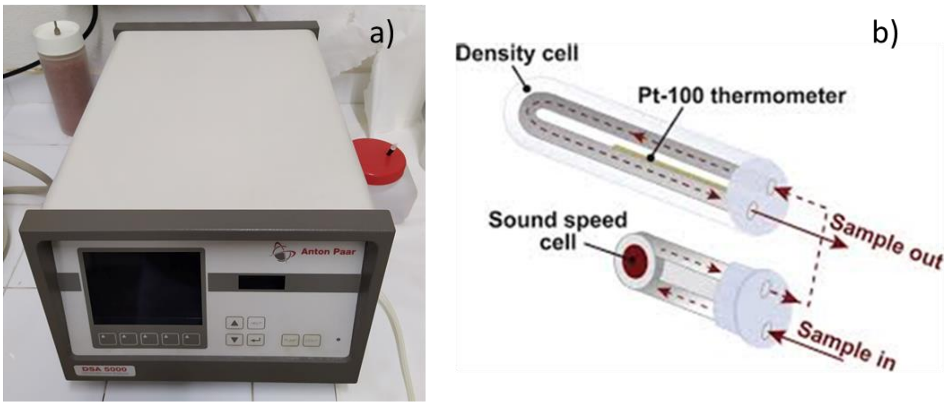


Figure 2.20 Anton Paar DSA 5000 densimeter: a) device and b) operation scheme of measuring cells.

2.5.3. Anton Paar rheometer Physica MCR 101

In this PhD Thesis, the rheological behavior of some nanodispersions was analyzed with a rotational rheometer Anton Paar Physica MCR 101 (Figure 2.21), which has a cone-plate geometry, with a cone diameter of 25 mm and a cone angle of 1º. Rheological tests can be mainly classified into rotational or oscillatory analysis. Flow tests are used to study the viscosity dependence with shear rate (pseudoplastic or dilatant behaviors) or with the time (thixotropic or rheopectic behaviors). This device allows controlling torques between (0.5 to $125 \cdot 10^3$) μN·m and normal forces from 0.1 to 30 N, with resolutions of 0.002 μN·m and 0.02 N, respectively [27]. The measurement procedure consists in applying shear stress to the sample and recording the corresponding shear rate. This device has a Peltier P-PTD 200 device (Anton Paar, Graz, Austria) that control the temperature with an uncertainty of 0.02 K. In our case, tests were performed only to check if the boron based nanodispersions had Newtonian or non-Newtonian behavior. For this aim, flow curves for base oil and hexagonal boron nitride nanodispersions were performed at low temperature (283.15 K) using controlled shear stress operation mode. The experiments were carried out during a research stay in the Applied Physics Department from the University of Vigo

Figure 2.21 Anton Paar Rheometer Physica MCR 101.

2.6. TRIBOLOGICAL CHARACTERIZATION

This section describes the different equipment that has been used to determine the coefficient of friction obtained lubricating steel specimens with the base oils and the studied nanodispersions, as well as the different ways to quantify the wear produced on the specimens during the tribological tests. In this way it can be known if the addition of nanoparticles to the oils produces anti-friction and/or anti-wear improvements for a possible use of the nanodispersion as lubricant in the industry.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

2.6.1. Tribo-cell coupled with Anton Paar rheometer

A modular compact rheometer (Anton Paar MCR302, Figure 2.22) equipped with a tribology cell (Tribo-cell T-PTD200) was utilized in order to obtain the friction coefficient of some nanodispersions and base oils. Moreover, this apparatus is also coupled with a Peltier hood H-PTD 200 which controls the temperature of the measuring system. This setup allows for measurements in a temperature range from 233.15 K to 573.15 K. This tribology cell has the ball on-three-pins configuration (Figure 2.21), which contains an upper tribological specimen that is a rotating chrome steel ball (100Cr6 steel and 12.7 mm of diameter) and a fixed lower specimen, which contains three chrome steel pins (100Cr6 and 6 mm in both diameter and height) in the sample holder as it is presented in Figure 2.22b. The ball is fixed on a shaft and driven by the MCR rheometer motor, then rotating on the three pins under a fixed axial force. This axial force, F, is transferred into three normal forces, F_N acting perpendicular to the bottom pins at the contact points, due to the ball presses the three pins (see figure 2.23) [28]. From the torque required to maintain the sliding speed, the frictional force, is obtained [29]. The flexibility of the bottom pins is required to get the same normal force acting evenly on all the three contact points of the upper ball. The rotating ball is adjusted automatically, and the forces are equally distributed on the three friction contacts. From figure 2.23 it can be concluded that the relation between the normal force F_N acting on the three pins and the axial force F of the rheometer is:

$$F_N = \frac{F}{3 \times \cos\alpha} \quad (2)$$

where α y the angle of the surface of the pins with the horizontal, which is 45º.

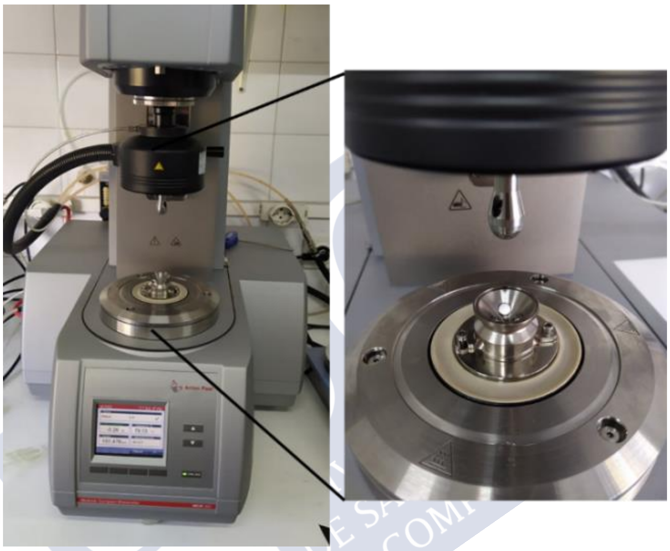


Figure 2.22 a) Anton Paar MCR302 rheometer b) equipped with a tribology cell (Tribo-cell T-PTD200).

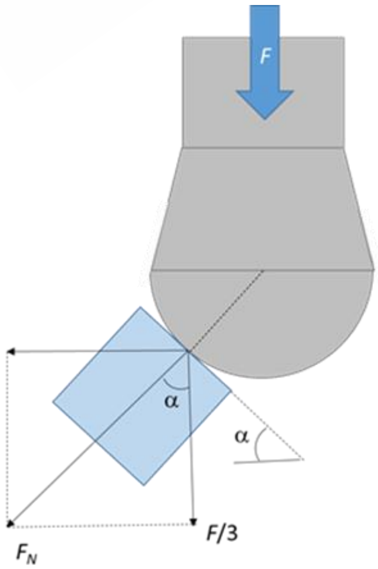


Figure 2.23 Ball-on-three pins friction measurement principle. Only one of the three pins is showed.

The sliding speed ranges from 10^{-8} m/s to 1.4 m/s. Before each test a 'zero-gap measurement' is carried out, in which the ball is lowered by the rheometer until softly touches the sample surface. The height at which the axial force is sensed corresponds to zero height. During the tribological tests, the pins were fully submerged by the addition of 1.3 mL of lubricant, an axial force of 45 N was applied resulting in a normal force of 21.21 N in each pin surface obtaining a maximum contact pressure around 1 GPa (mean contact pressure of 0.7 GPa). A constant sliding speed of 0.1 m/s was selected for a sliding distance test of 340 m and a fixed temperature of 293.15 K. In order to obtain rigorous results three replicates of each lubricant concentration were tested. Moreover, in addition both balls and pins have been cleaned with hexane and then dried with air before performing tests Through the Rheocompass Professional software, the apparatus provides the friction coefficient as a function of time during the tests.

2.6.2. CSM Standard Tribometer

Tribological tests were also carried out in a CSM Standard (CSM Instruments: Peseux, Switzerland) tribometer with ball-on-disk (Figure 2.24a) or reciprocating ball-on-plate (Figure 2.24b) configurations. For this aim, the specimen's material for the ball-on-disk configuration was chrome steel balls AISI 52100/535A99 (diameter: 6 mm; roughness 0.05 µm R_a), hardness: 58–66 Rockwell "C" Scale), which were run against AISI 52100/535A99 circular stainless steel plates (diameter: 10 mm; surface finish 0.02 µm R_a; hardness: 190–210 Hv30). On the other hand, for reciprocating ball-on-plate mode, chrome steel balls AISI 52100 (diameter: 6 mm; hardness: 803 HV; roughness < 0.032 µm R_a) were run against AISI 420 stainless steel plates (40.5 × 21 × 5 mm^3; hardness: 194 HV) with a mirror finish polishing (roughness, R_a, lower than 0.11 µm). Before starting a test, the ball and the plate were cleaned in hexane and dried with warm air. Then, the ball was introduced and tightly fixed the tribometer holder in order to achieve a pure sliding contact with the plate or the disk. The plate (or the disk) was placed and fixed in the lower part of the tribometer. For the reciprocating mode, the plate has a simple harmonic movement being the wear scar linear whereas in the case of ball on plate configuration the plate rotates being the wear scar a circle. The plates and the disks were lubricated with five drops of the lubricant. All tests were performed at room temperature (~296 K) but with different conditions depending the used

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

tribometer configuration. For the ball-on-plate mode, tests were conducted under a normal load of 2.5 N that corresponds to a maximum contact pressure of 0.88 GPa, at a stroke length of 10 mm, speed of 0.10 $m \cdot s^{-1}$ and a sliding distance of 500 m. On the other hand, for the pin-on-disk tests were carried out under a normal load of 20 N that corresponds to a maximum contact pressure of 1.79 GPa, with a trajectory radius of 3 mm, speed of 0.10 $m \cdot s^{-1}$ and a sliding distance of 340 m. Normal force was applied by means of calibrated loads. The CSM standard tribometer is equipped with a LVDT (linear variable differential transformer) sensor which provides high accuracy and precision for the force tangential measurement and hence the friction coefficient. The ball is mounted on a stiff lever, designed as a frictionless force transducer. Thus, tangential force was determined by the LVDT sensor measuring very small deflections of the lever. The tribometer send a signal to the computer, which is recorded and converted by the software in the friction coefficient during time for each lubricant. At least three replicates were performed for each lubricant to achieve more consistent results. After each tribological test, the specimens were rinsed with a stream of hexane for a few seconds.

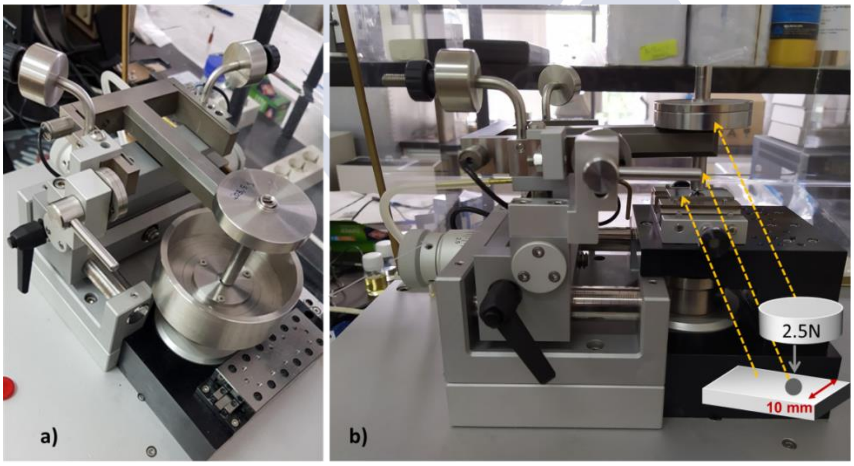


Figure 2.24 CSM Standard tribometer with a) ball-on-disk and b) reciprocating ball-on-plate measuring principles.

2.6.3. EHD2 Ultra Thin Film Measurement System

Film thickness measurements of lubricants were carried out using a ball-on-disc test apparatus (PCS Instruments, model EHD2) equipped with optical interferometry (Figure 2.25). The load-applying system is based on moving a carbon chrome steel ball of ¾ inch (19.05 mm of diameter) against a rotating glass disk which is coated with approximately 20 nm of chromium and 500 nm of silica layers (Figure 2.25). The disc and the steel ball are controlled by two electric motors to perform tests under rolling/sliding conditions, working at loads from 0 to 50 N, which leads to contact pressures until 0.7 GPa. The system measures the wavelength of the light returned from the central plateau of the contact and hence calculates the central film thickness, from 1 to 1000 nm. In addition, the instrument can measure lubricant film thickness down to 1 nm with a precision of 1 nm and works from room temperature to 423.15 K. Before each film thickness test, the zero distance is evaluated. The ball is loaded against the disc (same load as the test load), without lubricant between the disc and the ball. The space layer coating thickness is then evaluated through interferometry. The corresponding wavelength is recorded and set as the zero point. Measured wavelengths above that value means that the film thickness is higher than zero, below that value mean the space layer is worn out. This device was also utilized aiming to determine the friction coefficients of prepared nanolubricants and base oils. For this task, we use the same ball as that used in the film thickness measurements and two chrome steel discs (100 mm diameter) with different roughness each one (a polished disc, R_a =0.1 and a rough disc, R_a =0.5 μm). The applied load generates contact pressures up to 1.11 GPa. The normal load is measured with a load cell, positioned below the ball carriage, measuring the normal load applied on the ball against the disc. The friction force is also measured on the ball, through a torque cell mounted on the ball shaft with the disc rotating faster than the ball, and afterwards, at the slide-roll ratio (SRR), the friction force is measured again with the ball rotating faster than the disc. Therefore, the friction coefficient is then calculated from the normal force and the friction force. For both measurements, lubricant film thickness and friction coefficient tests, the measuring system was under fully flooded lubrication (130 mL of lubricant sample) and for three operating temperatures (303.15, 323.15 and 353.15 K). Traction coefficients can be measured at any slide/roll ratio from pure rolling up to 100%. In our case, both tests (film thickness and friction) were performed at 5% SRR with an entrainment speed ranging from 0.04 to 2 m s^{-1}.

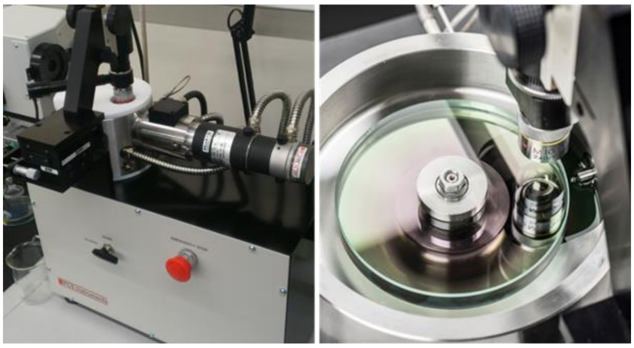


Figure 2.25 EHD2 tribometer.

2.6.4. Rolling bearing test rig

A modified Four-Ball machine was employed in order to carry out the rolling bearing tests using the configuration that is presented in Figure 2.26. Marques et al. [30] have modified the original machine replacing the four-Ball configuration by a rolling bearing assemble to test different type of rolling bearings. This new apparatus consists of two different parts: the first one is connected directly to the machine shaft and in the second part is the place where the bearing system is fitted. About 50 mL of sample guarantees that the lubricant level reaches the middle of the rollers according to the manufacturer's recommendation. SKF 51107 thrust ball bearings were used for these studies. The friction torque and operating temperature were uninterruptedly measured during the tests, the friction torque being measured with a piezoelectric torque cell KISTLER 9339 that ensured high-accuracy measurements even at very low friction torque. On the other hand, the temperature was measured by five thermocouples that measure the temperature at different strategic locations: inside the bearing assembly in real time, near to the rolling bearing and the lubricant and in the surrounding environment.

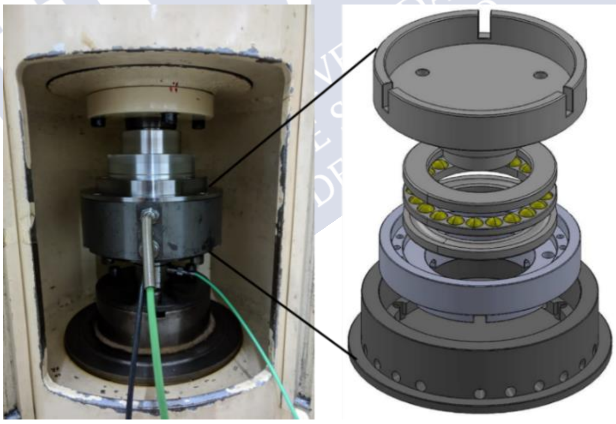


Figure 2.26 Modified Four-ball Machine.

2.6.5. 3D Optical Profilometer Sensofar S Neox

In order to quantify the wear that was produced in plates, disks and balls during the tribological tests of nanolubricants and base oils, a 3D Optical Profiler Sensofar (Terrassa, Spain) S Neox (Figure 2.27) was used. Moreover, this apparatus was also utilized to measure the roughness of the worn surfaces of plates and disks. This equipment can work in three different modes: confocal, interferometry and focus variation mode; the use of each one will depend on the conditions of the sample to be analyzed, such as the inclination of the surface, the transparency or the roughness. In addition, for each mode it has three different objectives (10x, 20x and 50x). This device is equipped with four LED sources (red, green, blue and white) within its core, used individually to optimize lateral resolution or optical coherence length. S Neox apparatus achieves vertical and lateral resolutions of 0.01 nm and 0.1 µm, respectively. The system additionally allows the acquisition of real 3D microscopy images as well as thickness measurements of any transparent coatings on the surface. This device includes personalization software (SensoMap), which combines surface data obtained by imaging and metrology instruments of different types. The most popular surface texture parameters are included in the analysis software, making the S neox compliant with ISO 25178. For the measurements of this PhD Thesis, confocal mode with a 10x objective was used to analyze the wear scar produced on the plates and balls surface lubricated with both, the base oils and the nanolubricants. The confocal mode owns a vertical resolution of 25 nm and a maximum slope of 14º when a 10x objective is employed. Wear was evaluated for plates in terms of the wear track width (WTW), wear track depth (WTD), transversal area and roughness. Roughness was determined in accordance with the ISO4287 standard (International Organization for Standardization, Vernier, Switzerland), applying a Gaussian filter with a long wavelength cut-off of 0.25 or 0.08 mm. In addition, scanning electron microscope (SEM) analyses were performed on the worn surface of plates to examine their morphology. For this purpose, a Carl Zeiss Ultraplus FESEM was utilized.

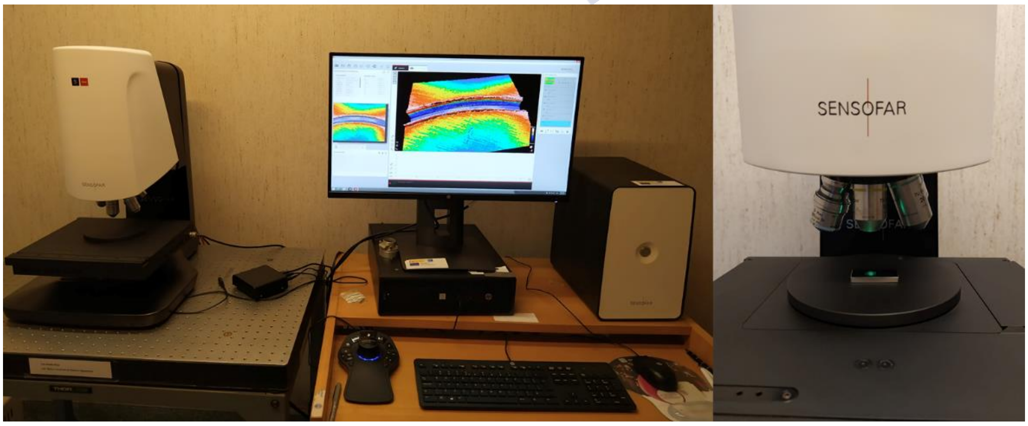


Figure 2.27 3D Optical Profiler Sensofar S Neox.

2.7. BIBLIOGRAPHY

[1] I. Otero, Thermophysical and tribological properties of ionic liquids as neat lubricants and as additives of biodegradable base oils for renewable energies, PhD Thesis, University of Santiago de Compostela, 2014.
[2] L.R. Rudnick, S.Z. Erhan, Synthetic, Mineral Oils and Bio-based Lubricants, 2nd Edition. CRC Press Taylor and Francis Group, London, 2013.
[3] S. Qiao, Y. Shi, X. Wang, Z. Lin, Y. Jiang, Synthesis of Biolubricant Trimethylolpropane Trioleate and Its Lubricant Base Oil Properties, Energy & Fuels 31 (2017) 7185-7190.
[4] A. Young, S. Bair, Experimental investigation of friction in entrapped elastohydrodynamic contacts, Tribology International 43 (2010) 1615-1619.
[5] Y. Wu, W. Li, M. Zhang, X. Wang, Improvement of oxidative stability of trimethylolpropane trioleate lubricant, Thermochimica Acta 569 (2013) 112-118.
[6] T.-S. Chang, R. Yunus, U. Rashid, T.S.Y. Choong, D.R. Awang Biak, A.M. Syam, Palm Oil Derived Trimethylolpropane Triesters Synthetic Lubricants and Usage in Industrial Metalworking Fluid, Journal of Oleo Science 64 (2015) 143-151.
[7] S.U. Ilyas, R. Pendyala, N. Marneni, Preparation, Sedimentation, and Agglomeration of Nanofluids, Chemical Engineering & Technology 37 (2014) 2011-2021.
[8] Y. Li, J.e. Zhou, S. Tung, E. Schneider, S. Xi, A review on development of nanofluid preparation and characterization, Powder Technology 196 (2009) 89-101.
[9] L. Kong, J. Sun, Y. Bao, Preparation, characterization and tribological mechanism of nanofluids, RSC Advances 7 (2017) 12599-12609.
[10] W. Yu, H. Xie, A review on nanofluids: preparation, stability mechanisms, and applications, Journal of Nanomaterials 2012 (2012) 1-17.
[11] J.A. Eastman, S.U.S. Choi, S. Li, W. Yu, L.J. Thompson, Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles, Applied Physics Letters 78 (2001) 718-720.
[12] M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, A. Amigo, J. Fernández, Thermophysical properties of polyalphaolefin oil modified with nanoadditives, The Journal of Chemical Thermodynamics 131 (2019) 192-205.
[13] J.P. Vallejo, E. Álvarez-Regueiro, D. Cabaleiro, J. Fernández-Seara, J. Fernández, L. Lugo, Functionalized graphene nanoplatelet nanofluids based on a commercial industrial antifreeze for the thermal performance enhancement of wind turbines, Applied Thermal Engineering 152 (2019) 113-125.
[14] J. Sanes, M.-D. Avilés, N. Saurín, T. Espinosa, F.-J. Carrión, M.-D. Bermúdez, Synergy between graphene and ionic liquid lubricant additives, Tribology International 116 (2017) 371-382.
[15] S. Mukherjee, S. Paria, Preparation and Stability of Nanofluids-A Review, IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE) 9 (2013) 63-69.
[16] S. Mukherjee, P.C. Mishra, P. Chaudhuri, Stability of Heat Transfer Nanofluids – A Review, ChemBioEng Reviews 5 (2018) 312-333.
[17] M. Ivanov, O. Shenderova, Nanodiamond-based nanolubricants for motor oils, Current Opinion in Solid State and Materials Science 21 (2017) 17-24.
[18] M.T. López-López, P. Kuzhir, G. Bossis, P. Mingalyov, Preparation of well-dispersed magnetorheological fluids and effect of dispersion on their magnetorheological properties, Rheologica Acta 47 (2008) 787-796.

[19] V. Khare, M.-Q. Pham, N. Kumari, H.-S. Yoon, C.-S. Kim, J.-I.L. Park, S.-H. Ahn, Graphene–Ionic Liquid Based Hybrid Nanomaterials as Novel Lubricant for Low Friction and Wear, ACS Applied Materials & Interfaces 5 (2013) 4063-4075.
[20] H.P. Mungse, O.P. Khatri, Chemically Functionalized Reduced Graphene Oxide as a Novel Material for Reduction of Friction and Wear, The Journal of Physical Chemistry C 118 (2014) 14394-14402.
[21] Y. Li, J. Zhao, C. Tang, Y. He, Y. Wang, J. Chen, J. Mao, Q. Zhou, B. Wang, F. Wei, J. Luo, G. Shi, Highly Exfoliated Reduced Graphite Oxide Powders as Efficient Lubricant Oil Additives, Advanced Materials Interfaces 3 (2016) 1600700.
[22] N.F. Azman, S. Samion, Dispersion Stability and Lubrication Mechanism of Nanolubricants: A Review, International Journal of Precision Engineering and Manufacturing-Green Technology 6 (2019) 393-414.
[23] A. Ghadimi, R. Saidur, H.S.C. Metselaar, A review of nanofluid stability properties and characterization in stationary conditions, International Journal of Heat and Mass Transfer 54 (2011) 4051-4068.
[24] M.J.G. Guimarey, M.R. Salgado, M.J.P. Comuñas, E.R. López, A. Amigo, D. Cabaleiro, L. Lugo, J. Fernández, Effect of ZrO_2 nanoparticles on thermophysical and rheological properties of three synthetic oils, Journal of Molecular Liquids 262 (2018) 126-138.
[25] M.J.G. Guimarey, Thermophysical Characterization of Lubricants Additivated with Nanoparticles for their Application in Renewable Energies, PhD Thesis, University of Santiago de Compostela, 2019.
[26] F.M. Gaciño, T. Regueira, L. Lugo, M.J.P. Comuñas, J. Fernández, Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids, Journal of Chemical & Engineering Data 56 (2011) 4984-4999.
[27] D. Cabaleiro, M.J. Pastoriza-Gallego, M.M. Piñeiro, L. Lugo, Characterization and measurements of thermal conductivity, density and rheological properties of zinc oxide nanoparticles dispersed in (ethane-1,2-diol+water) mixture, The Journal of Chemical Thermodynamics 58 (2013) 405-415.
[28] P. Heyer, J. Läuger, Correlation between friction and flow of lubricating greases in a new tribometer device, Lubrication Science 21 (2009) 253-268.
[29] F. Moreira-Izurieta, A. Jabbarzadeh, Tribological studies in cartilaginous tissue of lamb synovial joints lubricated by distilled water and interstitial-fluid-like solution, Tribology in Industry 39 (2017) 319-328.
[30] P.M.T. Marques, R.C. Martins, J.H.O. Seabra, Experimental measurement of rolling bearing torque loss in a modified Four-Ball machine: An improved setup, Lubrication Science (2020).

3 RESULTS and DISCUSSION

This section includes the full description and the general discussion of the results obtained in this PhD Thesis. The performed studies contain stability, thermophysical and tribological analyses for several studied nanolubricants. Following are detailed the results of this work. Subsections 3.1 and 3.2 list the publications in international journals and communications and proceedings presented at scientific conferences, respectively, directly derived from the results of this PhD Thesis. Other publications related with this work are summarized in subsection 3.3. Subsections 3.4-3.8 include for each of the published articles the objective, a brief description of the research and its main conclusions, followed by the corresponding original paper. A general discussion of the results obtained is provided in subsection 3.9.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

3.1. PUBLICATIONS DERIVED DIRECTLY FROM THIS PHD THESIS

The following articles published in peer-reviewed scientific Journals reports most of the results of this PhD Thesis:

A1. José M. Liñeira del Río, María J.G. Guimarey, María J.P. Comuñas, Enriqueta R. López, Alfredo Amigo, Josefa Fernández. Thermophysical and tribological properties of dispersions based on graphene and a trimethylolpropane trioleate oil. J. Mol. Liquids 2018, 268, 854-866. DOI: https://doi.org/10.1016/j.molliq.2018.07.107

Editorial: ELSEVIER SCIENCE BV, ISSN: 0167-7322.

Copyright, subsection *Personal use: "Authors can use their articles, in full or in part, for a wide range of scholarly, non-commercial purposes as outlined below:"* including in these points *"Inclusion in a thesis or dissertation (provided that this is not to be published commercially)"* (https://www.elsevier.com/about/policies/copyright)

A2. José M. Liñeira del Río, María J. G. Guimarey, María J.P. Comuñas, Enriqueta R. López, Jose I. Prado, Luis Lugo, Josefa Fernández. Tribological and Thermophysical Properties of Environmentally-Friendly Lubricants Based on Trimethylolpropane Trioleate with Hexagonal Boron Nitride Nanoparticles as an Additive. Coatings 2019, 9, 509. DOI:http://dx.doi.org/10.3390/coatings9080509

Editorial: MDPI, ISSN: 2079-6412.

Copyright and Licensing: "For all articles published in MDPI journals, copyright is retained by the authors", "In addition, the article may be reused and quoted provided that the original published version is cited" and *"These conditions allow for maximum use and exposure of the work, while ensuring that the authors receive proper credit."* (https://www.mdpi.com/authors/rights).

A3. José M. Liñeira del Río, Enriqueta R. López, Josefa Fernández, Fátima García. Tribological properties of dispersions based on reduced graphene oxide sheets and trimethylolpropane trioleate or PAO40 oils. J. Mol. Liquids 2019, 274, 568-576.

DOI: https://doi.org/10.1016/j.molliq.2018.10.107

Editorial: ELSEVIER SCIENCE BV, ISSN: 0167-7322.

Copyright, subsection *Personal use: "Authors can use their articles, in full or in part, for a wide range of scholarly, non-commercial purposes as outlined below:"* including in these points *"Inclusion in a thesis or dissertation (provided that this is not to be published commercially)"* (https://www.elsevier.com/about/policies/copyright)

A4. José M. Liñeira del Río, Enriqueta R. López, Josefa Fernández. Synergy between boron nitride or graphene nanoplatelets and tri(butyl) ethylphosphonium diethylphosphate ionic liquid as lubricant additives of triisotridecyltrimellitate oil. J. Mol. Liquids 2020, 301, 112442

DOI: https://doi.org/10.1016/j.molliq.2020.112442

Editorial: ELSEVIER SCIENCE BV, ISSN: 0167-7322.

Copyright, subsection *Personal use: "Authors can use their articles, in full or in part, for a wide range of scholarly, non-commercial purposes as outlined below:"* including in these points *"Inclusion in a thesis or dissertation (provided that this is not to be published commercially)"* (https://www.elsevier.com/about/policies/copyright)

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

A5. José M. Liñeira del Río, Enriqueta R. López, Manuel González Gómez, Susana Yáñez Vilar, Yolanda Piñeiro, José Rivas, David E.P. Gonçalves, Jorge H.O. Seabra and Josefa Fernández. Tribological behavior of nanolubricants based on coated magnetic nanoparticles and trimethylolpropane trioleate base oil. Nanomaterials 2020, 10, 683 DOI: https://doi.org/10.3390/nano10040683

Editorial: MDPI, ISSN: 2079-4991.

Copyright and Licensing: "For all articles published in MDPI journals, copyright is retained by the authors", "In addition, the article may be reused and quoted provided that the original published version is cited" and *"These conditions allow for maximum use and exposure of the work, while ensuring that the authors receive proper credit."* (https://www.mdpi.com/authors/rights).

3.2. Communications presented at scientific conferences

The main results of this PhD Thesis were presented in the following conferences and meetings:

C1. M. Piñeiro Fiel, E.R. López, M.J.G. Guimarey, J.M. Liñeira del Río, M.J.P. Comuñas, M. Reichelt, J. Fernández. Tribological properties of trimethylolpropane trioleate-zirconia based nanolubricants. IX Iberian Conference on Tribology, Guimarães (Portugal), June 12-13, 2017.

C2. J.M. Liñeira, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, A. Amigo, J. Fernández. Propiedades termofísicas y tribológicas de nanolubricantes. V Encontro da Mocidade Investigadora, Santiago de Compostela (Spain), June 12-13, 2017.

C3. M.J.P. Comuñas, E.R. López, A. Amigo, M.J.G. Guimarey, J.M. Liñeira, J. Fernández. Desarrollo de Lubricantes Basados en Nanoaditivos para la Producción de Energías Renovables y uso Eficiente de la Energía. XXXVI Reunión Bienal de la Real Sociedad Española de Física, Santiago de Compostela (Spain), July 17-21, 2017.

C4. J.M. Liñeira, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, A. Amigo, J. Fernández. Caracterización termofísica de nanolubricantes basados en grafeno y trioleato de trimetilolpropano. XXXVI Reunión Bienal de la Real Sociedad Española de Física, Santiago de Compostela (Spain), July 17-21, 2017.

C5. J.M. Liñeira del Río, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, A. Amigo, J. Fernández. Thermophysical properties of nanolubricants based on a biodegradable oil and

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

graphene or boron nitride. 21st European Conference on Thermophysical Properties, Graz (Austria), August 3-8, 2017.

C6. J.M. Liñeira del Río, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, J. Fernández. Propiedades tribolóxicas de nanolubricantes de nitruro de boro en polialfaolefina. VI Encontro da Mocidade Investigadora-Ciencias, Santiago de Compostela, (Spain), May 30-31 2018.

C7. J.M. Liñeira del Río, E.R. López, J. Fernández, F. García, D. Peña. Highly Exfoliated Reduced Graphene Oxide Based Nanolubricants 8th International Seminar on Thermodynamic Engineering of Fluids, Tarragona (Spain), July 25-26, 2018.

C8. J.M. Liñeira del Río, E.R. López, J. Fernández. Graphene Derivatives and Ionic Liquids as Additives in Synthetic and Mineral Oils. 3rd REGALIS Autumn School, Santiago de Compostela (Spain), November 5-8, 2018.

C9. J.M. Liñeira del Río, E.R. López, J. Fernández. Lubricants based on graphene or boron nitride nanoadditives, a phosphonium ionic liquid and a biodegradable base oil. Ibertriva 2019: X Iberian Conference on Tribology, Ibertrib, XI Iberian Vacuum Conference, Seville (Spain), June 25-28, 2019.

C10. J.M. Liñeira del Río, E.R. López, J. Fernández, F. García. Tribological behavior of reduced graphene oxide based nanolubricants. Ibertriva 2019: X Iberian Conference on Tribology, Ibertrib, XI Iberian Vacuum Conference, Seville (Spain), June 25-28, 2019.

C11. J.M. Liñeira del Río, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, J.I. Prado, L. Lugo, J. Fernández. Tribological and thermophysical properties of eco-friendly lubricants containing hexagonal boron nitride nanoparticles. Ibertriva 2019: X Iberian Conference on Tribology, Ibertrib, XI Iberian Vacuum Conference, Seville (Spain), June 25-28, 2019.

C12. J. Fernández, E.R. López, J.M. Liñeira del Río. Ionic liquids as lubricant additives. Synergies with nanoparticles. V International Conference of ionic liquid-based materials, Paris (France), November 4-8, 2019.

3.3. COMPLEMENTARY PUBLICATIONS

In relation with one of the base oils of this Thesis (trimethylolpropane trioleate, TMPTO) and other base oils and formulated lubricants, viscosity-pressure coefficients and film thickness calculations were made in the following articles and communications:

CP1. José M. Liñeira del Río, María J.G. Guimarey, María J.P. Comuñas, Josefa Fernández. High pressure viscosity behaviour of tris(2-ethylhexyl) trimellitate up to 150 MPa. J. Chem. Thermodynamics 138, 2019, 159–166
DOI: https://doi.org/10.1016/j.jct.2019.06.016

CP2. David E.P. Gonçalves, José M. Liñeira del Rio, María J.P. Comuñas, Josefa Fernández, Jorge H.O. Seabra. High Pressure Characterization of the Viscous and Volumetric Behavior of Three Transmission Oils. Ind. Eng. Chem. Res. 2019, 58, 4, 1732-1742. DOI: http://doi.org/10.1021/acs.iecr.8b05090.

CP3. J.M. Liñeira del Río, M.J.G. Guimarey, M.J.P. Comuñas, J. Fernández. Analysis of the high pressure viscosity of trioctyl trimellitate and trimethylolpropane trioleate. 21st European Conference on Thermophysical Properties. Graz (Austria), August 3-8, 2017

CP4. D.E.P. Gonçalves, J.M. Liñeira del Rio, M.J.P. Comuñas, J. Fernández, J.H.O. Seabra. Comportamiento volumétrico y viscoso de tres lubricantes comerciales a alta presión. XVI Encuentro Inter-Bienal del Grupo Especializado de Termodinámica (GET), Santa Cruz, Oleiros, A Coruña (Spain), September 16-18, 2018

CP5. D.E.P. Gonçalves, J.M. Liñeira del Rio, M.J.P. Comuñas, J. Fernández, J.H.O. Seabra. Viscous and volumetric behavior of three transmission oils under high pressure. Ibertriva 2019: X Iberian Conference on Tribology, Ibertrib, XI Iberian Vacuum Conference, Seville (Spain), June 25-28, 2019.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

3.4. THERMOPHYSICAL AND TRIBOLOGICAL PROPERTIES OF DISPERSIONS BASED ON GRAPHENE AND A TRIMETHYLOLPROPANE TRIOLEATE OIL

The article A1 focuses on the study of thermophysical and tribological properties of nanolubricants formed by a polyester base oil (TMPTO) and graphene nanoplatelets (GnP) as additives. For this purpose, four nanolubricants with different mass concentrations (0.05 wt %, 0.10 wt%, 0.25 wt% and 0.5 wt%) of GnP were prepared using the two-step method. Before studying thermophysical and tribological properties of the nanolubricants, their temporal stability against sedimentation was evaluated through visual observation and dynamic light scattering techniques, during time, observing that the time stability (~ 96 h) was bigger than the required to carry out the analyses. Thermophysical properties (density, viscosity and speed of sound) at atmospheric pressure were analyzed for the four prepared nanolubricants and for the base oil. Density and viscosity increase with the addition of GnP whereas the speed of sound slightly decreases when concentration increases. Viscosity is the property more affected by the addition of GnP, achieving increases around 11% for the highest concentration (0.5 wt%) respect to the TMPTO base oil. Specifically, at 278.15 K the viscosity for TMPTO is 248 mPa s whereas for 0.5 wt% nanolubricant a value of 276 mPa s was obtained. On the other hand, density also increases when the mass concentration grows but less than the viscosity. At 278.15 K the density of the base oil is 0.9263 g cm^{-3} whereas for the most concentrated nanolubricant in GnP the density is 0.9290 g cm^{-3}, which leads to a density increment of 0.29%. Regarding to the speed of sound, a small decrease is observed when the mass concentration of nanoparticles increases. For the base oil (at 283.15 K) a 1501.5 m s^{-1} value is found while for the most concentrated nanolubricant the speed of sound is 1500.5 m s^{-1} which corresponds to a tiny decrease of 0.067%. These three properties were successfully correlated as functions of both temperature and volume fraction by means of simple empirical equations. Tribological behavior of prepared nanolubricants was analyzed. For this aim, the reciprocating ball-on-plate tribometer was utilized, working at room temperature and under a load of 2.5 N. For lubricated steel/steel contacts, the friction coefficient is decreased with each one of all the prepared nanolubricants respect to that obtained with base oil, obtaining the best performance with the nanolubricant containing 0.50 wt% in GnP. Precisely, the lowest coefficient of friction obtained is 0.105 (for 0.50 wt%) and for the base oil is 0.163, which leads to a friction reduction of 36%. As regards to the

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

produced wear, it was evaluated as the wear track width (WTW). This parameter is reduced, in comparison to that obtained with base oil, using the nanolubricants with 0.10 and 0.25 wt% in GnP, being the optimal nanolubricant that with 0.25 wt%, which leads to a reduction of 4%. Then it can be concluded that the best anti-wear and anti-friction nanolubricant is that containing 0.25 wt% in GnP.

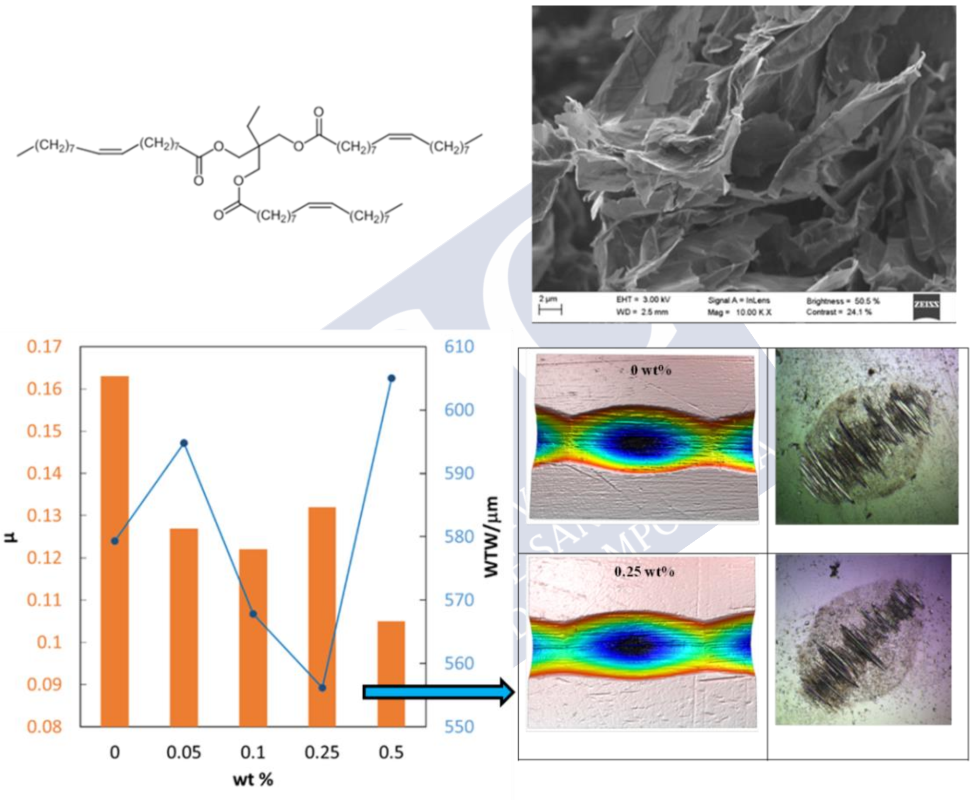


Figure 3.1 Graphical abstract for article A1

3.5. Tribological and Thermophysical Properties of Environmentally-Friendly Lubricants Based on Trimethylolpropane Trioleate with Hexagonal Boron Nitride Nanoparticles as an Additive

In the publication A2 thermophysical (density and viscosity), rheological and tribological properties of nanolubricants formed by a polyester base oil (TMPTO) and hexagonal boron nitride nanoparticles (h-BN) were studied. For this aim, three nanolubricants with different mass concentrations (0.5 wt%, 0.75 wt% and 1 wt%) of h-BN were formulated using the two-step method. Subsequently, their stability time against sedimentation was evaluated by visual observation and dynamic light scattering during time, obtaining that the time stability (~24 h) was larger than the needed to perform the tribological and thermophysical studies. Thermophysical properties (density, viscosity, viscosity index) and rheological behavior at atmospheric pressure were evaluated for the three formulated nanolubricants. Density slightly grows when h-BN concentration increases, with densities for the 1 wt.% nanolubricant being over 0.6% higher than those for TMPTO. These values were effectively correlated as a function of both temperature and mass concentrations. On the other hand, the viscosities of nanolubricants are higher than those of the base fluid across the entire temperature range, being 9.2% the maximum increase. Nonetheless, the viscosities of the nanodispersion containing 1 wt.% of h-BN are slightly smaller than those of the 0.75 wt.% concentration at temperatures lower than 323 K. Considering the expanded (k=2) uncertainty of the viscometer (1%), viscosity values are compatible with the expected viscosity-h-BN loading trend. As regards to viscosity index this parameter grows with the addition of nanoparticles obtaining the following data: 189.7, 191.7, 193.3 and 194.4 for the base oil and 0.50, 0.75, and 1.0 wt.% of h-BN, respectively. In relation to rheological measurements at low temperature (283.15 K) nanolubricants show Newtonian performance apart from 1 wt.% of h-BN at low shear rates, which slightly shows a typical shear-thinning behavior with viscosity decreasing with growing shear rate. Tribological behavior of studied nanolubricants was examined. For this task, a reciprocating ball-on-plate tribometer was employed, working under a load of 2.5 N and at room temperature. The friction coefficient values for all nanolubricants are lower than that corresponding to the base oil, obtaining the best behavior for the nanolubricant of 0.75 wt% in h-BN. Specifically, the lowest coefficient of friction obtained is 0.122 (for 0.75 wt%) and for the base oil is 0.163. In relation to the produced wear, this parameter was evaluated in terms of the maximum width (WTW) and depth (WTD), and the transversal area of the wear tracks. The best anti-wear behavior was achieved for the nanolubricant containing 0.75 wt.% of h-BN, which reduced the WTW by 9%, the WTD by 14%, and the transversal area by 22% in comparison with the TMPTO base oil. Considering these results and friction behavior, the best anti-friction and anti-wear capability was reached with the 0.75 wt% nanolubricant. A smoother surface was obtained when the tribological contact was lubricated with this last nanolubricant instead of with the neat oil. This fact was confirmed by measuring the roughness (R_a) and analyzing the worn surfaces through SEM images and confocal Raman spectroscopy. With the last technique an important h-BN presence in the worn surface was found, indicating the formation of boundary tribofilm between lubricating surfaces.

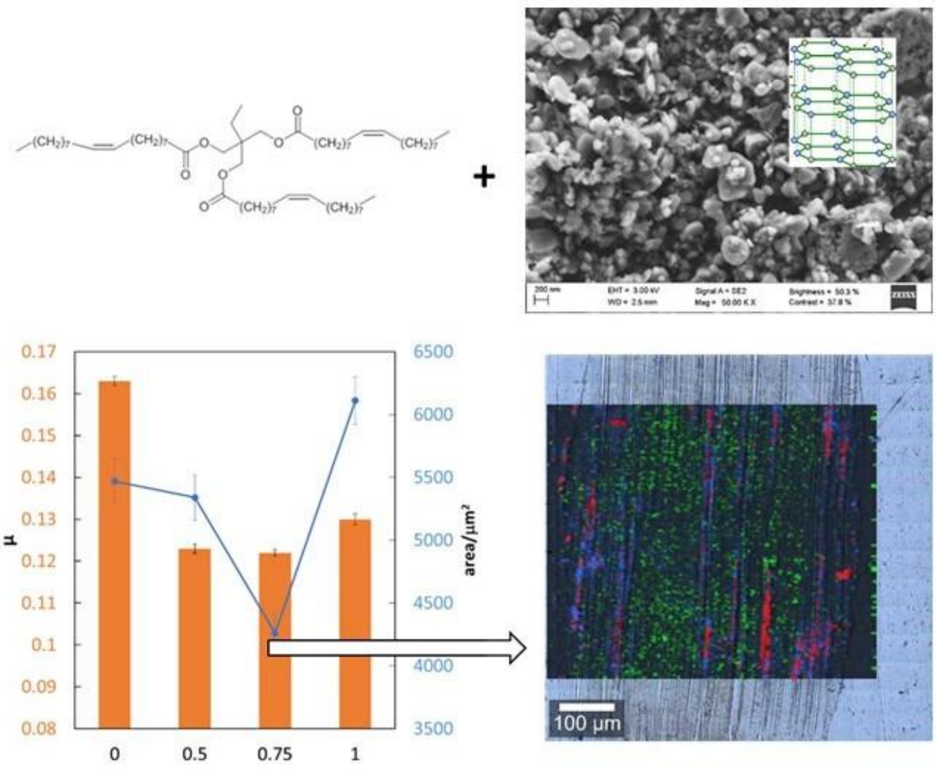


Figure 3.2 Graphical abstract for article A2

3.6. TRIBOLOGICAL PROPERTIES OF DISPERSIONS BASED ON REDUCED GRAPHENE OXIDE SHEETS AND TRIMETHYLOLPROPANE TRIOLEATE OR PAO40 OILS

The article A3 focuses on the study of tribological behavior of nanolubricants formed by reduced graphene oxide (rGO) nanoparticles and two different type of base oils: a polyester (TMPTO) and a polyalphaolefin (PAO40). For this purpose, rGO nanopowders were obtained by thermal reduction of graphene oxide (GO) powders using KOH/ethanol as reducing agent. A complete characterization through different techniques was done in order to check that the chemical modification occurred successfully, observing that rGO nanoparticles only presents 7% of oxygen content while GO had 33%. Four nanolubricants with different mass concentrations of rGO (0.05 wt %, 0.10 wt%, 0.25 wt% and 0.5 wt%) were prepared using a two-step method. Through reduction of these nanosheets, a good stability against sedimentation was achieved (~240 h) which was much higher than the required time to complete the tribological measurements. Tribological performance of nanolubricants was studied. For this purpose, a pin-on-disk tribometer was used at room temperature with a load of 20 N. The friction coefficient was for all the nanolubricants lower than that obtained with base oils. In the case of TMPTO nanolubricants, the best friction coefficient was obtained for the nanolubricant based on TMPTO with a 0.25 wt% in rGO. Specifically, a friction coefficient of 0.0721 was obtained for this optimal concentration against 0.0904 for the neat TMPTO oil, which leads to a 20% friction reduction. As regards to the wear, WTW is reduced for all the studied nanolubricants in comparison with the TMPTO base oil, obtaining a maximum wear reduction (24%) for the concentration of 0.25 wt% rGO. Therefore, the use of rGO at this concentration greatly enhances the anti-friction and anti-wear capabilities respect to those of the base oil. On the other hand, for PAO40 nanolubricants the best friction coefficient was also achieved for the nanolubricant with a 0.25 wt% in rGO. Precisely, a friction coefficient of 0.0715 was obtained for this optimal concentration against 0.0944 for the neat PAO40 oil, which leads to a 24% friction reduction. Relating to the wear, wear track widths of rGO nanolubricants based on PAO40 are similar for all concentrations. A smoother surface was obtained when the disks were lubricated with 0.25 wt% in rGO nanolubricant instead of with the TMPTO base oil. Moreover, through confocal Raman spectroscopy on the worn surface of the disks, rGO nanosheets were found, confirming physical adsorption of rGO in the worn area, forming a boundary tribofilm between contact surfaces.

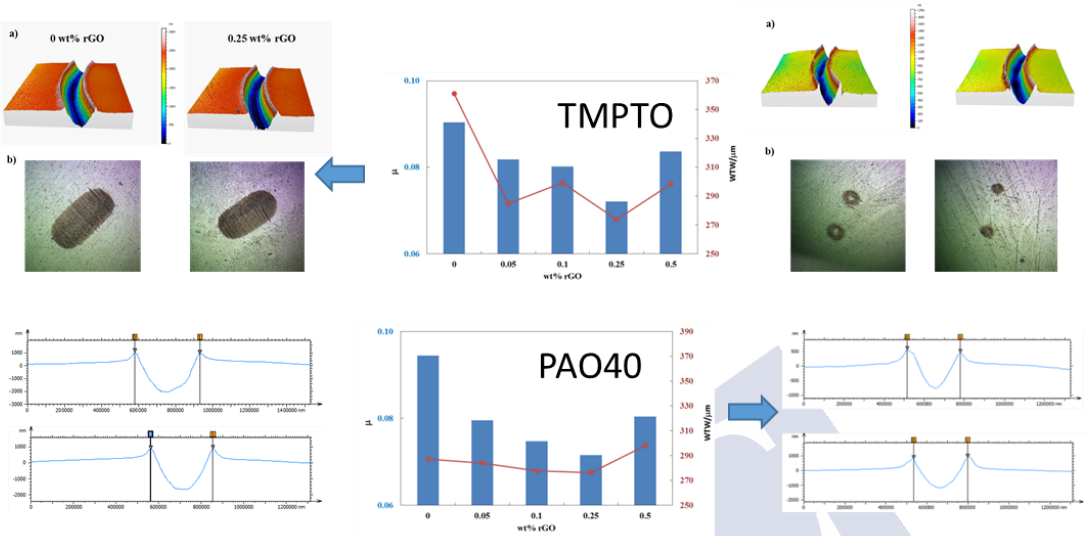


Figure 3.3 Graphical abstract for article A3

3.7. SYNERGY BETWEEN BORON NITRIDE OR GRAPHENE NANOPLATELETS AND TRI(BUTYL) ETHYLPHOSPHONIUM DIETHYLPHOSPHATE IONIC LIQUID AS LUBRICANT ADDITIVES OF TRIISOTRIDECYL TRIMELLITATE OIL

In the article A4 thermophysical (density and viscosity) and tribological properties of different nanolubricants containing an ionic liquid (IL) were studied. These nanolubricants are formed by graphene nanoplatelets, GnPs, or nanosheets of hexagonal boron nitride, h-BN, with or without the IL tri(butyl) ethylphosphonium diethylphosphate ($[P_{4,4,4,2}][C_2C_2PO_4]$) in an ester type base oil, triisotridecyltrimellitate (TTM). Four dispersions were prepared apart from a mixture of TTM and $[P_{4,4,4,2}][C_2C_2PO_4]$ with a concentration of 2 wt% of the IL. Two-step method was used to make the nanodispersions TTM + 0.1 wt% h-BN and TTM + 0.1 wt% GnP. To prepare TTM + 2 wt% IL + 0.1 wt% h-BN and TTM + 2 wt% IL + 0.1 wt% GnPs nanodispersions a different method was applied. Firstly, h-BN or GnP nanopowders were added to the IL and then this blend was mechanically mixed in an agate mortar during 5 min and finally sonicated by ultrasounds. Before studying thermophysical and tribological properties of nanolubricants their stability against sedimentation was estimated through visual observation and the evolution of refractive index during time, observing that the time stability (>3 weeks) was larger than the needed to perform the analyses. Thermophysical properties (density and viscosity) at atmospheric pressure were evaluated for five dispersions and for the base oil. Both properties, hardly rises with the addition of additives (IL and/or nanoparticles) respect to base oil. The higher values for density and viscosity were achieved with the nanolubricant TTM/IL/GnP. Thus, the maximum growth in density respect to TTM is about 0.23% at 368.15 K whereas in the case of viscosity the maximum increase is 6.7% at 373.15 K. On the other hand, tribological properties of nanolubricants were studied. For this reason, a pin-on-disk tribometer was used, working under a load of 20 N and at room temperature. Friction coefficients achieved with each one of the four nanodispersions and the IL mixture are lower than that corresponding using TTM without additives. The lowest friction coefficient was found for the nanolubricant TTM/IL/GnP, 0.0836, against 0.125 for the base oil. This result leads to a friction reduction of 33%. Concerning the wear, all the prepared dispersions present low wear than the base oil without additives, being the best wear reduction for the nanolubricant TTM/IL/GnP with a 44% reduction in WTW and 66% in average cross-sectional area respect to base oil without additives.

Smoother surfaces were obtained when the disks were lubricated with each one of the lubricants instead of TTM, being the bigger roughness reduction for TTM/IL/GnP nanolubricant. Specifically, a R_a of 7.0 nm was obtained against a R_a of 19.7 for the TTM base oil, which leads to a 65% reduction. Consequently, mending effect takes place resulting in a smoother surface. Moreover, Raman analysis on the worn surface of the disks lubricated with the studied dispersions were carried out, obtaining that boundary tribofilms between contact surfaces were formed.

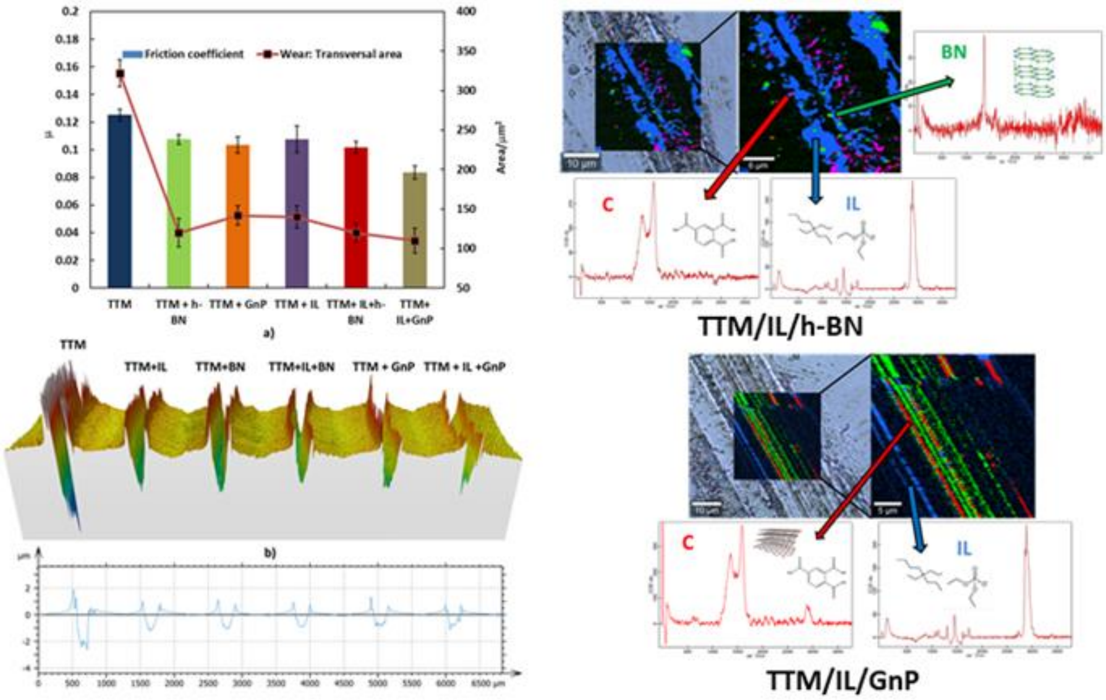


Figure 3.4 Graphical abstract for article A4

3.8. Tribological behavior of nanolubricants based on coated magnetic nanoparticles and trimethylolpropane trioleate base oil

The article A5 focuses on the study of tribological performance of nanolubricants formed by trimethylolpropane trioleate (TMPTO) base oil with superparamagnetic nanoparticles: Fe_3O_4 (6.3 nm), Fe_3O_4 (10 nm) and Nd alloy (19 nm), all of them coated with oleic acid. For this aim, the nanoparticles were synthesized, by NanoMag group, via chemical co-precipitation or thermal decomposition by adsorption with oleic acid. Three nanolubricants with the mass concentration of 0.015 wt% in Fe_3O_4 of two different sizes (6.3 nm and 10 nm) and Nd alloy (19 nm) magnetic nanoparticles were prepared using a modified two-step method.

The nanoparticles were dispersed in cyclohexane after their synthesis and then, they were transferred to chloroform. Subsequently, concentration of nanodispersions is determined by thermogravimetry and the chloroform dispersion was added to the TMPTO base oil and mixed by ultrasonic agitation. Finally, the chloroform was eliminated from the oil using a rotary evaporator. Temporal stability of nanolubricants against sedimentation was evaluated through visual observation and refractometry techniques, during time, observing that the time stability (at least eleven months) is much higher than the required to perform the analyses. Thermophysical properties (density and viscosity) at atmospheric pressure were studied for all nanolubricants and for base oil. Both properties hardly vary with the addition of magnetic nanoparticles respect to base oil. The higher values for density and viscosity were achieved with the Nd alloy nanolubricant. Specifically, the maximum density and viscosity increases are only 0.2 and 2.8 %, respectively, which were obtained with the later alloy at 278.15 K in comparison to the base oil. As regards to tribology, two different types of tribological tests were carried out: pure sliding conditions and rolling conditions (5 % slide to roll ratio). For the former test, a ball on three pins configuration was used, being the friction coefficients for the three nanolubricants lower than that achieved with the base oil, being the best friction performance obtained with the Nd alloy nanolubricant with a friction reduction of 29 % in comparison to TMPTO base oil. The obtained wear values (diameter, depth and volume) at these conditions for the three nanolubricants are lower than that corresponding to the base oil, obtaining the maximum wear reductions for the Nd alloy nanolubricant, being 67 % and 35 % in terms of diameter and depth of the wear scar, respectively. A smoother surface was obtained when the pins are lubricated with each one of the nanolubricants instead of with the base oil, being the bigger roughness reduction for Nd alloy nanolubricant. Specifically, a R_a of 37.3 nm was obtained against a R_a of 60.9 for the TMPTO base oil, which leads to a 54% reduction. Consequently, polishing and mending effects take place due to the presence of nanoparticles. Moreover, Raman analysis in the worn pins lubricated with the studied dispersions were conducted, obtaining that mending, polishing and boundary tribofilm effects on contact surfaces occur. On the other hand, at rolling conditions of 5 % SRR and 30 ºC, Stribeck curves for all lubricants are similar while at higher temperatures the Fe_3O_4 (6.3 nm) nanolubricant shows lower friction coefficient in comparison to the base oil and the other nanolubricants. In addition, friction torque tests were carried out observing that Fe_3O_4 (6.3 nm) nanolubricant leads to a lower friction torque in comparison with the base oil, especially at low speeds.

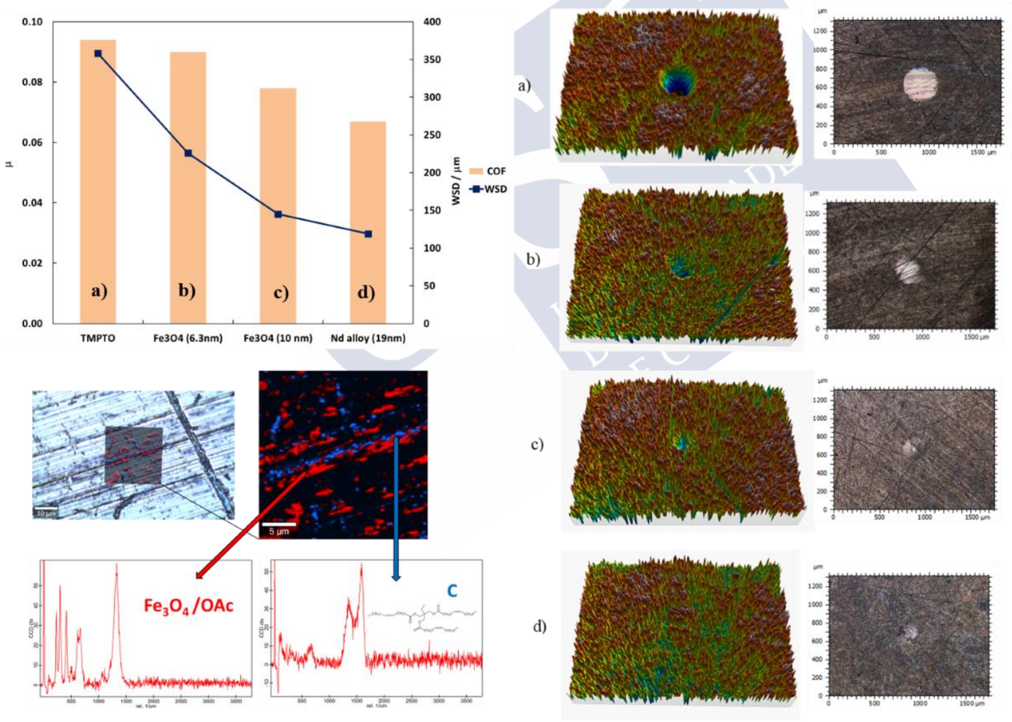


Figure 3.5 Graphical abstract for article A5

3.9. GENERAL DISCUSSION

At the beginning of this PhD Thesis the stability time of numerous combinations of nanolubricants were studied through visual observation, these nanolubricants are formed by base oils and formulated oils in combination with different nanoparticles (Tables 2.1 and 2.2). Most of the lubricant + nanoadditive combinations were discarded because of the very low stability time. Other combinations were rejected due to the bad antifriction and/or anti-wear behavior. For instance, nanolubricants based on Priolube 1936 (a petrochemical diester) with h-BN nanoparticles (0.25, 0.5, 0.75 and 1 wt%) as additives showed friction coefficients, which are between 5 to 18% higher than the base oil. Moreover, nanodispersions based on Priolube 1936 and GnP (0.05, 0.1, 0.25 and 0.5 wt%) increase the friction coefficients from 2 to 25%. On the other hand, dispersions composed by the formulated oil Castrol Tribol 1510 and GnP (0.05, 0.1, 0.25 and 0.5 wt%) showed similar friction results to the oil without nanoplatelets, being the produced wear higher than that produced by the oil without GnPs. No appreciable friction reductions were found using dipentaerythritol tetraalkanoates DiPEC5, DiPEC7 with h-BN as additive. It is interesting to remark that although microparticles of mica and kaolin present not large stability time, reductions in the friction coefficient and wear up to 24% and 21% were obtained, respectively. For PAO40/GnP dispersions the obtained friction reductions were lower than 21% but wear was just reduced up to 3%. PAO40/h-BN nanodispersions lead to similar friction capabilities but better wear reductions (33%). All these preliminary results were reported in several conferences (see communications C1-C3 and C5 in section 3.2)

Taking into account all the initial stability and tribological results, nanolubricants formed by TMPTO and h-BN or GnP nanopowders (Table 3.1) were selected to study their tribological performance in a first step. In the case of nanolubricants formed by TMPTO and GnP friction and wear reductions of 36% and 13%, respectively, for 0.5 wt% GnP nanolubricant in comparison to the base oil (Table 3.2) were found. As regards nanolubricants formed by TMPTO and h-BN, 25% reductions in both friction and wear were found for 0.75 wt% h-BN nanolubricant (Table 3.2). These results are remarkably good but the stability times were 48 and 98 hours for h-BN and GnP nanolubricants, respectively.

In order to achieve nanolubricants with a better stability in a second step the use of chemically modify nanoparticles was analyzed. For this aim, GO nanoparticles were chemically reduced through a thermal treatment to rGO nanoparticles, which have good stability (Table 3.1). Tribological behavior of rGO nanolubricants based on TMPTO and PAO40 base oils were studied. For TMPTO nanolubricants reductions of 20% in friction and wear were observed for 0.25wt% rGO in comparison to base oil. On the other hand, for PAO40 nanolubricants reductions of 24 and 15 % in friction and wear, respectively, were found for 0.25 wt% in rGO (Table 3.2). In this case, rGO nanoadditives improve not only the tribological capabilities of both base oils but also lead to the time stability higher than the previous nanolubricants: up to 148 hours.

Table 3.1 Time stability of the selected nanolubricants.

Base Oil	Nanoparticle	Time stability
TMPTO	h-BN	48 hours
	GnP	96 hours
	rGO	148 hours
	Fe_3O_4-OA (6.3 nm)	> eleven months
	Fe_3O_4-OA (10 nm)	> eleven months
	Nd alloy-OA (19nm)	> eleven months
PAO40	GO	< 24h
	rGO	148 hours
TTM	h-BN	48 hours
	GnP	96 hours
	h-BN +IL	Three weeks
	GnP + IL	Three weeks

Analyzing the aforementioned results, in a third step two different strategies were studied:

a) Study the effect of adding an ionic liquid to nanolubricants and analyze the possible improvements in stability time as well as the possible synergies between ionic liquid and nanoparticles in the antifriction and anti-wear behavior. For this purpose, the ionic liquid tri(butyl) ethylphosphonium diethylphosphate was added to the nanolubricants formed by the TTM base oil and nanoparticles of h-BN or GnP. TTM was chosen due to its polarity, biodegradability and its viscosity degree, appropriate for gear oils. As regards the time stability, an important improvement was achieved in comparison to nanolubricants without IL (Table 3.1). Respecting to the tribological behavior, positive synergies were found for the two nanolubricants containing IL. Specifically, the best antifriction and anti-wear behavior was obtained for the nanolubricant formed by GnP nanoparticles (0.1 wt%) and IL (2 wt%) with reductions of 33 and 44% in friction and wear, respectively (Table 3.2).

b) Testing the tribological performance of nanolubricants with new nanoadditives coated with oleic acid. Superparamagnetic nanoparticles with an oleic acid coating were used: Fe_3O_4 (6.3 nm), Fe_3O_4 (10 nm) and Nd alloy (19 nm). In this case, TMPTO was selected in order to compare with the aforementioned results. These coated nanoparticles were combined with TMPTO base oil obtaining amazing stability times for eleven months (Table 3.1). Regarding to their tribological performance, reductions in friction and wear were obtained for all nanolubricants respect to the base oil (Table 3.2). Precisely, for the Nd allow nanolubricant maximum reductions of 29 and 67% were observed in friction and wear, respectively. Moreover, rolling conditions tests were utilized to study friction and film thickness of these nanolubricants, obtaining that Fe_3O_4 (6.3 nm) nanolubricant reduces friction in comparison to TMPTO.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Table 3.2 Tribological results of the selected nanolubricants and the TTM+ IL mixture.

Base Oil	Nanoadditive	% Friction reduction	% Wear reduction(WTW)
TMPTO	h-BN	25% (0.75wt%, 2.5N)	9% (0.75wt%, 2.5N)
	GnP	36% (0.50wt%, 2.5N)	4% (0.25wt% 2.5N)
	rGO	20% (0.25wt%, 20N)	20% (0.25wt%, 20N)
	Fe_30_4 (6.3 nm)	4% (0.015wt%, 10N)	37% (0.015wt%, 10N)
	Fe_30_4 (10 nm)	18% (0.015wt%, 10N)	59% (0.015wt%, 10N)
	Nd alloy (19nm)	29% (0.015wt%, 10N)	67% (0.015wt%, 10N)
PAO40	rGO	24% (0.25 wt%, 20N)	15% (0.25 wt%, 20 N)
TTM	h-BN	14% (0.1 wt%, 20N)	28% (0.1 wt%, 20N)
	GnP	17% (0.1wt%, 20N)	30% (0.1wt%, 20N)
	IL	14% (2wt%, 20N)	32% (2wt%, 20N)
	h-BN +IL	19% (0.1 + 2 wt%, 20N)	35% (0.1 + 2 wt%, 20N)
	GnP + IL	33% (0.1 + 2 wt%, 20N)	44% (0.1 + 2 wt%, 20N)

USC
UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

4. CONCLUSIONS and PERSPECTIVES

The main conclusions that follow from the results described in the previous chapters, regarding the objectives of this PhD Thesis, are:

1. As regards the selection, synthesis and characterization of nanoadditives to obtain suitable nanolubricants, both h-BN and GnP nanoadditives were selected and reduced graphene oxide and three superparamagnetic nanoparticles (two magnetites and one Nd alloy coated with oleic acid) were synthetized. The size of the nanoadditives was determined with TEM, ranging from 6.3 nm for one of the coated magnetites to 70 nm for h-BN nanoparticles. The thickness of the rGO nanosheets is between 0.7 and 1.2 nm. The oxygen content of reduced graphene oxide, obtained with Raman spectroscopy, is 7%. The oleic acid content in the used magnetic nanoparticles as well as the number of oleic acid molecules per surface area of each nanoparticle were estimated by NanoMag group, being the later 1 for the Nd Alloy and 5 for the magnetite of 6.3 nm.

2. Respect to the obtention of stable dispersions of nanoadditives in some synthetic lubricant bases, through chemical surface modification of nanoparticles and the use of ionic liquids, excellent results were found. Thus, reduced graphene oxide leads to the time stability of nanolubricants up to 148 hours, which is higher than the previous nanolubricants (from 12 to 96 h). When tri(butyl) ethylphosphonium diethylphosphate (IL) was used, the stability time of the nanolubricants increases up to three weeks. Finally, with the coated magnetic nanoparticles the stability increases up to eleven months.

3. As regards to the thermophysical characterization of some nanolubricants: density, both dynamic and kinematic viscosity, and viscosity index were measured for

nanolubricants based on TMPTO with (0.05, 0.10 and 0.25) wt% of GnP and with (0.50, 0.75 and 1.0) wt% of h-BN, as well as on TTM with GnP (0.1 wt%) or h-BN (0.1 wt%) nanoparticles with or without IL (2 wt%). As regards TMPTO nanolubricants, density slightly increased as the concentration of nanoparticles in the nanolubricant increased, up to 0.62% (1.0 wt% of h-BN), whereas the viscosity increment reached 11% (0.50 wt% of GnP). The viscosity index hardly varies, being the maximum increase of 2.5% (for the 1.0 wt.% of h-BN nanolubricant). Concerning the lubricants based on TTM and GnP or h-BN nanoparticles with or without IL, density and viscosity slightly rise with the addition 2 wt% of the IL in comparison to base oil. The highest density and viscosity values were obtained with the TTM/IL/GnP nanolubricant with increases of 0.23 and 9.6% in density and viscosity, respectively.

4. Respect to the tribological behavior (friction and wear) of the potential designed nanolubricants in boundary lubrication regime, we have found the following results:

a) Influence of weight concentration was evaluated for nanolubricants based on TMPTO with (0.05, 0.10 and 0.25) wt% of GnP, with (0.50, 0.75 and 1.0) wt% of h-BN and with (0.05, 0.10, 0.25 and 0.50) wt% of rGO as well as those based on PAO40 with (0.05, 0.10, 0.25 and 0.50) wt% of rGO. The friction coefficient was for all the nanolubricants lower than that obtained with TMPTO, but for some concentrations the wear was not improved for the three kinds of nanoadditives. For the TMPTO/GnP dispersions, the maximum friction reduction (36%) was reached by the 0.50 wt% nanolubricant whereas the minimum wear width by the 0.25 wt% nanolubricant (4% reduction). On the other hand, for the TMPTO/h-BN dispersions, the best anti-friction and anti-wear capability was achieved with the 0.75 wt% nanolubricant. Thus, reductions of 25% in the friction coefficient, 9% in the case of the wear scar, 14% of the scar depth, and 22% of the transversal area, were obtained with respect to the base oil. h-BN was found by Raman spectroscopy in the worn surfaces tested with the nanolubricants indicating polishing, mending and protective tribofilm effects. Regardless the base oil the highest antifriction and antiwear (WTW) reductions were obtained for the dispersions with 0.25 wt% in rGO, being, respectively, 20% and 20% for TMPTO nanolubricants and 24% and 15 % for PAO 40. From the confocal Raman spectroscopy on wear tracks of the plates, we can conclude that there is physical adsorption of the rGO nanopowders on the steel surfaces.

b) Influence of size of the nanoadditives in the tribological behavior was evaluated for nanolubricants based on TMPTO with 0.015 wt% of Fe_3O_4-OA (6.3 nm) or Fe_3O_4-OA (10 nm) at boundary conditions. The highest antifriction and antiwear (WSD) reductions were obtained for the dispersions with coated Fe_3O_4 (10 nm,), being respectively 18% and 59%, which are quite bigger than those obtained with Fe_3O_4 (6.3 nm) (4% and 37%, respectively). Interestingly, better friction and antiwear reductions, 29% and 67%, were obtained using a coated Nd alloy (19 nm). The depths of the wear scar obtained with the three nanolubricants are lower than those corresponding to the base oil, obtaining maximum depth wear reductions of 35% for the Nd alloy nanolubricant. Protective tribofilm formation, mending and polishing effects were confirmed by confocal Raman microscopy on the worn surfaces for these three coated nanoparticles.

5. Concerning the evaluation of some nanolubricants for elastohydrodynamic lubrication, film thickness of nanolubricants based on TMPTO with 0.015 wt% of Fe_3O_4 (6.3 nm), Fe_3O_4 (10 nm) and Nd alloy (19 nm) are very similar due to their similar viscosities, therefore the lubrication capacity will be analogous for all lubricants. Under rolling conditions of 5% SRR, the full Stribeck curves for all lubricants are similar whereas at high temperatures the Fe_3O_4 (6.3 nm) nanolubricant shows lower friction coefficient than the base oil and the other nanolubricants. Moreover, Fe_3O_4 (6.3 nm) nanolubricant leads to a lower friction torque in comparison with the base oil, especially at low speed when the film is thin and the nanoparticles play an important role in the reduction of friction.

6. The synergies of anti-friction nanoadditives with tri(butyl) ethylphosphonium diethylphosphate were analyzed studying the tribological performance of lubricants based on TTM with GnP (0.1 wt%) or h-BN (0.1 wt%) nanoparticles with or without this IL. The mean friction coefficients obtained lubricating the contacts with each one of the dispersions TTM/GnP/IL or TTM/h-BN/IL are lower than the corresponding ones using TTM without additives. A maximum friction reduction of 33% with the TTM/IL/GnP nanodispersion was obtained. Wear was evaluated in terms of the width (WTW), the depth (WTD) and cross-section area of the wear track, as well as the roughness of the worn surface. In comparison to those obtained with the base oil, maximum reductions of WTW (44%), transversal area (66%) and mean roughness (65%) correspond to the TTM/IL/GnP nanodispersion whereas

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

the maximum reduction of WTD (32%) is obtained with TTM/IL/h-BN. Thus, it can be concluded that positive synergies between the IL and h-BN or GnP as additives of TTM were evidenced. Tribofilm formation, mending and polishing effects were confirmed by confocal Raman microscopy on the worn surfaces.

7. Finally, the main objective of this PhD Thesis was achieved, because several nanolubricants formed by the addition of nanoparticles in some esters and PAO base oils were designed and characterized. This fundamental study can contribute to provide knowledge to the industry on lubricants that can be used in real applications improving the currently used lubricant performance as well as proposing higher performance environmentally friendly lubricants. This PhD Thesis involves both features. On the one hand, most of the studies performed involves green alternative oils, as TMPTO. On the other hand, polyalphaolefins (PAO) are currently used as lubricants in different applications as wind turbines gearboxes.

Regarding *future work and perspectives*, it should be indicated that:

a) Positive synergies between GnP or h-BN and a phosphonium based ionic liquid were found as hybrid additives of TTM. These results are an excellent starting point for future researches. Evaluation of these hybrid nanolubricants for elastohydrodynamic lubrication through Stribeck curves, film thickness and friction torque measurements is envisaged.
b) Furthermore, the study of the possible synergies between PAOs and these hybrid additives, or others based on different phosphonium LIs, is also envisaged. In addition, combine two different nanoadditives with or without an ionic liquid is another interesting possibility that should be also investigated.
c) The positive tribological results of this PhD Thesis, obtained with the nanolubricants based on neat PAOs additivated with the different investigated 2D nanomaterials (h-BN, GnP or rGO) encourage us to analyze the synergies of anti-friction nanoadditives with the additives contained in three commercial lubricants based on PAOs, formulated for gearboxes, but poor stability times were found. Thus, more studies concerning this issue were initially discarded. Nevertheless, it would be very interesting to undertake future

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

researches aimed at elucidating whether these hybrid additives are a feasible alternative to those currently used as friction modifiers.

d) Taking into account the noticeable positive results obtained in this PhD Thesis using functionalized nanoparticles with ester base oils, other remarkable future study is to use this method to improve commercial lubricants currently used in gears and engines.

e) Finally, to characterize the magneto-rheological behavior of the nanolubricants containing superparamagnetic nanoparticles is another attracting research because they could be used as smart lubricants due to their elastrohydrodynamic behavior can be changed varying the magnetic field.

USC
UNIVERSIDADE
DE SANTIAGO
DE COMPOSTELA

USC
UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

APPENDIX

Resumen

Actualmente, uno de los mayores retos científico-tecnológicos es la planificación del comportamiento de consumo y ahorro a largo plazo, e intentar equilibrarlos de la mejor manera posible. En términos económicos, las pérdidas totales anuales originadas por contactos tribológicos se estiman en 2,536,000 millones de euros, siendo el 73% debido a la fricción y el 27% debido al desgaste. Las pérdidas por fricción y desgaste pueden reducirse sustancialmente mediante el uso de nuevas soluciones tribológicas. Entre estas nuevas soluciones se encuentra el diseño de nuevos lubricantes, con una mejor interacción con las superficies que lubrican, con el fin de optimizar las prestaciones tribológicas de los mismos. Así, el control y la mejora continua de la lubricación es, sobre todo desde el punto de vista económico, de gran importancia en la industria. Los lubricantes son substancias formadas por una base de aceite y un pequeño porcentaje de aditivos que tienen diversas funciones como: lubricar, refrigerar y proteger superficies en movimiento relativo, minimizando el contacto entre las mismas y, por tanto, el desgaste. A la hora de seleccionar un lubricante se deben considerar numerosos factores como el rango de temperatura en el que va a operar, la carga a la que va a estar sometido, los materiales y la velocidad relativa de las superficies a las que va a lubricar, así como otros aspectos como la estructura y el diseño de la propia máquina en la que se vayan a utilizar. Las bases de los lubricantes pueden ser de tres tipos, según el proceso de obtención (aceites minerales, sintéticos y vegetales). Los aditivos son también de diferentes clases dependiendo de la función que vayan a desempeñar (antiespumantes, antidesgaste, modificadores de viscosidad…), con el fin de que los lubricantes que los contienen sean óptimos para las diversas aplicaciones. Estos aditivos son compuestos orgánicos o inorgánicos, los cuales se encuentran disueltos o suspendidos en el aceite base al que aditivan. Con la continua evolución de la tecnología, es necesario diseñar nuevos lubricantes con mejores propiedades antifricción y antidesgaste que operen correctamente en sistemas de diferente tamaño, entre ellos sistemas microelectromecánicos y nanoelectromecánicos, para evitar pérdidas energéticas y por tanto económicas en toda la industria. Ante esta perspectiva, durante los últimos años surge la idea de usar nanomateriales como aditivos antifricción y antidesgaste, con el fin de lograr que estos aditivos mejoren estas capacidades de los aditivos tradicionales. Entre las principales ventajas de su uso aparecen la baja interacción química con otros aditivos; su capacidad para adherirse a las superficies y por tanto formar películas protectoras, su habilidad para penetrar en cualquier aspereza del material y por tanto ejercer una función de reparación, así como la gran resistencia que presentan a altas temperaturas de trabajo y su alta conductividad térmica.

A la hora de proponer nuevos nanolubricantes, una cuestión muy importante es estudiar el efecto que tiene la adición de nanomateriales a los aceites en sus propiedades termofísicas, ya que éstas afectarán a su rendimiento final. La principal propiedad que debemos estudiar es la viscosidad, ya que es una propiedad muy importante durante los regímenes elastohidrodinámico y mixto. Además, es de vital importancia conocer el índice de viscosidad de los lubricantes, el cual informa como varía esta viscosidad de los lubricantes con la temperatura, puesto que en los sistemas mecánicos se dan numerosos cambios de temperatura. Sin embargo, el factor más importante a tener en cuenta en el diseño de un potencial lubricante, es conocer cómo éste se va a comportar en relación a la fricción y desgaste que se va a producir entre los elementos mecánicos de un sistema lubricado, ya que lo que se busca principalmente en un buen lubricante es reducir el desgaste producido entre los contactos metálicos con el fin de tener un ahorro energético y por tanto económico.

El objetivo principal de esta Tesis Doctoral es diseñar y caracterizar nanolubricantes formados por la adición de nanomateriales en algunos ésteres y aceites base PAO en el marco de dos proyectos de investigación (ENE2014-55489-C2-1/2-R y ENE2017-86425-C2-1/2-R). Concretamente, se han empleado principalmente dos ésteres: trioleato de trimetilolpropano (TMPTO) y triisotridecil trimelitato (TTM) y una polialfaolefina (PAO 40). Los ésteres pertenecen al grupo V de la clasificación del American Petroleum Institute (API) mientras que la polialfaolefina pertenece al grupo IV de la misma. En el estudio preliminar para la selección de bases y nanoaditivos se han utilizado también varios aceites minerales, otros ésteres y siete lubricantes formulados comerciales diseñados para frenos y sistema hidráulico de aerogeneradores, así como para motores y cajas de cambio de automoción. Tanto los aceites base como los lubricantes formulados fueron donados por las empresas Repsol, Croda, Verkol y Enel Green Power, que asesoran al grupo de investigación en ambos proyectos.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

En cuanto a los nanomateriales que se emplearon como aditivos de los aceites base han sido adquiridos en la empresa Iolitec, donados por Nanoinnova Technologies, o sintetizados en la USC. Se han analizado principalmente nanopartículas de nitruro de boro hexagonal (h-BN), de óxido de grafeno (GO), de óxido de grafeno reducido (rGO), de magnetitas (Fe_3O_4) de distintos tamaños (6.3 y 10 nm), de una aleación de neodimio (Nd alloy, 19 nm) así como nanoplaquetas de grafeno (GnPs). Las nanopartículas de nitruro de boro hexagonal (h-BN) tienen un diámetro medio en torno a 70 nm y una densidad aparente de 2.29 g cm^{-3}, mientras que las nanoplaquetas de grafeno (GnP) tienen un tamaño medio de (11–15) nm y una densidad aparente de 2.25 g cm^{-3}. Asimismo, en el estudio preliminar, se han utilizado nanopartículas de óxidos de Níquel (II), Magnesio y hierro (II) (NiO, MgO, FeO), de mica y de caolín. Cabe mencionar que también se ha utilizado un líquido iónico, el tri(butil)etilfosfonio dietilfosfato, como aditivo dispersante.

Se ha llevado a cabo una completa caracterización de los aceites base, así como de las nanopartículas mediante diferentes técnicas: HPLC acoplado a espectrometría de masas, espectroscopia de infrarrojo (FTIR), espectroscopia Raman, microscopía electrónica de barrido (SEM), microscopía electrónica de transmisión (TEM), espectroscopia fotoelectrónica de rayos X (XPS), entre otros. Estos ensayos se han llevado a cabo en colaboración con el Servicio de Apoyo a la Investigación (RIAIDT) de la Universidad de Santiago de Compostela, el laboratorio NANOMAG, también de la Universidad de Santiago de Compostela, así como con el Centro de Apoio Científico-Tecnolóxico á Investigación (C.A.C.T.I.) de la Universidad de Vigo.

En lo que a la preparación de los nanolubricantes se refiere, durante esta Tesis Doctoral se ha utilizado un método de dos pasos para las nanodispersiones con GnP, h-BN, GO o rGO. En el caso de los lubricantes con líquido iónico se ha utilizado un método de dos pasos modificado, ya que los nanoaditivos y el LI se mezclan mecánicamente con ayuda de un mortero de ágata durante diez minutos. En lo que respecta a los nanolubricantes superparamagnéticos, las nanopartículas sintetizadas en un disolvente orgánico se añadieron al aceite base, eliminando este disolvente mediante ebullición, obteniendo de este modo los nanolubricantes con la ayuda de un rotavapor. Una microbalanza Sartorius MC 210P de alta precisión ha sido utilizada para determinar la concentración en masa de los componentes de los nanolubricantes. Con el objetivo de obtener nanodispersiones homogéneas se han empleado una punta de ultrasonidos (HD 2200 Sonopuls) y un baño de ultrasonidos

(Fisherbrand) para dispersar las nanopartículas en el aceite base. En el caso de la punta, las condiciones de sonicación utilizadas han sido: potencia (200 W), amplitud (302 μm), tipo de sonda y diámetro (MS73, 3 mm) y 1 h de tiempo de sonicación. Cabe decir que para evitar el sobrecalentamiento durante este proceso de las muestras se sumergieron en un baño de hielo. Por otra parte, para el baño de ultrasonidos se emplearon las siguientes condiciones: potencia efectiva de 180 W y frecuencia de agitación de 37 kHz, durante periodos continuos de 4 h.

Uno de los principales retos durante esta Tesis es la obtención de potenciales nanolubricantes estables durante largos periodos del tiempo para ser usados en la industria. Por este motivo, se ha realizado un profundo estudio de estabilidad de los mismos con diferentes técnicas. La técnica usada en primer término es el control visual y posteriormente si la estabilidad visual es buena se emplean otras técnicas como la refractometría o la dispersión dinámica de luz (DLS). Debido a los pobres resultados de estabilidad encontrados en el estudio preliminar, se han sintetizado varias nanopartículas modificadas químicamente, así como usado un líquido iónico como agente dispersante, con el objetivo de incrementar la estabilidad de los nanolubricantes.

Con respecto a la metodología usada para determinar propiedades termofísicas de los nanolubricantes, la densidad y viscosidad a presión atmosférica, la velocidad del sonido, el índice de viscosidad, así como las curvas de flujo de los aceites base y los nanolubricantes se determinaron experimentalmente usando un viscosímetro rotacional, dos densímetros de tubo vibrante así como un reómetro con geometría cono-plato.

En cuanto a los ensayos tribológicos se ha determinado el coeficiente de fricción y el desgaste producido principalmente en lubricación límite. Además, para los lubricantes superparamagnéticos se han realizado medidas de espesor de película de lubricante, curvas de Stribeck y medidas de par de fricción en rodamientos. Para realizar las medidas de coeficiente de fricción para lubricación límite se empleó un tribómetro en configuración bola sobre placa operando tanto en modo reciprocante como en rotacional y un reómetro acoplado a una celda tribológica con configuración bola sobre tres pines. Para analizar el desgaste producido durante estos ensayos se ha utilizado un perfilómetro óptico 3D, así como un microscopio electrónico de barrido. Se han estudiado los mecanismos de reducción de desgaste en las probetas de acero debido a los nanoaditivos y al líquido iónico mediante microscopía electrónica de barrido y microscopía Raman confocal, entre otras. En cuanto a la realización de las curvas de Stribeck y las medidas de espesor de película de lubricante, se ha utilizado otro tribómetro con configuración bola sobre disco. Finalmente, para las medidas de par de fricción, se ha utilizado una máquina de cuatro rodamientos.

En particular, en esta Tesis Doctoral se ha estudiado el comportamiento termofísico y tribológico de nanolubricantes basados en un aceite sintético de tipo éster, el (TMPTO) con 0.05, 0.10, 0.25 y 0.50 wt% de GnPs como aditivos. Para estos nanolubricantes, se estudió la dependencia con la temperatura y la concentración del nanoaditivo de distintas propiedades termofísicas (densidad, viscosidad y velocidad del sonido) a presión atmosférica. Viscosidad y densidad aumentan a medida que aumenta la concentración de nanopartículas y disminuyen con la temperatura, mientras que la velocidad del sonido disminuye ligeramente con la concentración de GnP. Por ejemplo, la adición de 0.5 wt% de nanoplaquetas de grafeno provoca un aumento en la densidad del 0.29 % en comparación al aceite base TMPTO. En cuanto a la viscosidad, para el mismo nanolubricante, se observó un incremento relativo de la viscosidad del 11.2%.

Se han llevado a cabo ensayos tribológicos para el TMPTO y los nanolubricantes de GnPs mencionados anteriormente. Para ello se ha empleado un tribómetro con configuración de bola sobre placa operando en modo reciprocante a temperatura ambiente y bajo una carga de 2.5 N. Se observó que el coeficiente de fricción para todos los nanolubricantes se reduce con respecto al del aceite base, teniendo un valor óptimo para la dispersión del 0.50 wt% de GnPs. El coeficiente de fricción más bajo fue 0.105, que se obtuvo para el nanolubricante con 0.50% en peso de GnP, y que es un 36% menor que el obtenido con el aceite sin aditivos, 0.163. El desgaste se cuantificó en términos del ancho de la huella de desgaste, obteniéndose pequeñas reducciones con respecto al obtenido con el TMPTO, para los nanolubricantes con 0.10 y 0.25 wt% en GnPs. Concretamente se observó una reducción máxima del 4% para el nanolubricante de 0.25 wt%. Por tanto, el mejor rendimiento antidesgaste y antifricción corresponde a esta concentración de 0.25 wt% en GnPs.

Se ha llevado a cabo el estudio del comportamiento termofísico y tribológico de nanolubricantes basados en el trioleato de trimetilolpropano (TMPTO) con 0.50, 0.75 y 1 wt% de nanopartículas de nitruro de boro (h-BN) como aditivos. Para estos nanolubricantes, se estudió la dependencia con la temperatura y la concentración de nanopartícula de distintas propiedades termofísicas, densidad y viscosidad a presión atmosférica, así como el comportamiento reológico. La densidad aumentó ligeramente con la concentración de nanopartículas en el nanolubricante, hasta un 0.62%. Los valores de densidad de los nanolubricantes y TMPTO se correlacionaron con éxito como función de temperatura y concentraciones en peso de nanopartículas. En cuanto a la viscosidad, esta propiedad aumentó para las nanodispersiones con respecto al aceite base, hasta un máximo de 9.2%. Además, se observó que el nanolubricante con la mayor concentración de nanopartículas, 1.0% en peso, mostró un comportamiento no newtoniano a 283.15 K y bajas velocidades de cizalla.

Se han llevado a cabo ensayos tribológicos para el TMPTO y para los tres nanolubricantes de h-BN. Para ello se ha empleado el tribómetro con configuración bola sobre placa en modo reciprocante a temperatura ambiente y bajo una carga de 2.5 N. Se observó que el coeficiente de fricción para todos los nanolubricantes se reduce con respecto al aceite base. En cuanto al desgaste se observaron mejoras para los nanolubricantes con 0.5 y 0.75 wt% en h-BN. La mejor capacidad antifricción y antidesgaste se logró con el nanolubricante con 0.75 wt% de h-BN. Así, se obtuvieron reducciones del 25% en el coeficiente de fricción, 9% en el caso del ancho de huella de desgaste, 14% para la profundidad y del 22% en el área transversal, con respecto al aceite base. Además, para estos lubricantes se analizaron los mecanismos de desgaste mediante espectroscopia Raman, observando nanopartículas de h-BN en las superficies desgastadas, concluyéndose que el buen desempeño tribológico de los nanolubricantes es debido a la combinación de los efectos de tribofilm, reparación y pulido.

Se han estudiado las propiedades tribológicas de los nanolubricantes formados por los aceites base trioleato de trimetilolpropano (TMPTO) o una polialfaolefina (PAO40) con nanopartículas de óxido de grafeno reducido (rGO). Para ello, en primer lugar, se ha realizado la reducción de las nanopartículas de óxido de grafeno (GO) con el fin de tener una buena estabilidad de los nanolubricantes. Para este objetivo, se prepararon nanopolvos de rGO por reducción térmica de óxido de grafeno usando una mezcla KOH/etanol como agente reductor, obteniendo rGO con solo un 7% de contenido en oxígeno. Se prepararon dispersiones de los aceites base TMPTO o PAO40 con (0.05, 0.10, 0.25 y 0.50) wt% de GO o rGO observando que a través de la modificación química de GO se obtienen nanodispersiones más estables (148 horas).

Para los dos aceites base y todos los nanolubricantes de rGO, se llevaron a cabo ensayos tribológicos con un tribómetro operando en configuración bola sobre disco en modo rotacional, bajo una carga de trabajo de 20 N a temperatura ambiente. Se observó que los

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

coeficientes de fricción de todos los nanolubricantes fueron inferiores a los de los aceites base. Concretamente el mejor comportamiento antifricción se obtuvo para los nanolubricantes de 0.25 wt% en rGO para los lubricantes de TMPTO y también para los de PAO40, teniendo reducciones de fricción del 20 y 24%, respectivamente. En cuanto al desgaste, para los nanolubricantes de TMPTO, se observaron disminuciones de desgaste para todos los nanolubricantes respecto del aceite base, con una reducción máxima del ancho de huella del 24% para el nanolubricante de 0.25 wt% en rGO. Por otra parte, para los nanolubricantes basados en PAO40, el desgaste apenas varía para las diferentes concentraciones, obteniendo una reducción máxima de 15% para la concentración de 0.25 wt%. Comparando los desgastes de los lubricantes formados por ambos aceites, se concluye que los basados en PAO40 producen un desgaste menor que los de TMPTO. Finalmente se analizó el papel que juegan los nanoaditivos en la reducción del desgaste, a través de espectroscopia Raman. En estos análisis se concluyó que existe adsorción física de las nanopartículas de rGO en la superficie desgastada.

Además, se estudiaron las sinergias entre un líquido iónico y nanopartículas como aditivos híbridos de lubricantes. Para este propósito, cuatro dispersiones basadas en GnP o h-BN con o sin el líquido iónico tri(butil)etilfosfonio dietilfosfato (IL) en un aceite base de tipo éster, triisotridecil trimelitato (TTM), se prepararon y se analizaron termofísica y tribológicamente como potenciales nanolubricantes. La concentración en peso de los nanoaditivos es del 0.1 wt%, mientras que para el IL es del 2 wt %. Se han logrado grandes resultados de estabilidad debido a la adición del IL, concretamente las dispersiones en las que estaba presente el IL fueron estables durante tres semanas. Los valores de densidad y viscosidad de los nanolubricantes muestran que ambas propiedades aumentan ligeramente con la adición de IL y/o nanoaditivos.

En lo que respecta a los ensayos tribológicos, se llevaron a cabo con un tribómetro operando en configuración rotacional de bola sobre disco bajo una carga de trabajo de 20 N a temperatura ambiente. Con respecto al aceite base, para la nanodispersión TTM/IL/GnP se obtuvo una reducción máxima de fricción de 33%. El mejor rendimiento antidesgaste también corresponde a esta misma nanodispersión con una reducción del ancho de la huella de desgaste del 44% y una fuerte disminución de la sección del área transversal del 65%, ambas respecto a las obtenidas con el aceite base TTM. En el caso de la profundidad de la huella de desgaste, la reducción máxima fue del 32% para la nanodispersión de TTM/IL/h-BN. Además, los valores de rugosidad de las superficies desgastadas lubricadas con las nanodispersiones TTM/IL/GnP y TTM/IL/h-BN son más bajos que los correspondientes al aceite puro, a la mezcla TTM/IL y a los de las dispersiones binarias correspondientes. Por lo tanto, se encontraron sinergias positivas entre el IL y los nanoaditivos de GnP o h-BN como aditivos híbridos de TTM. Finalmente, por medio de espectroscopia Raman se evidenció la formación de tribofilms protectores por parte de IL y nanoaditivos, y que el principal mecanismo mediante el que actúan estos nanomateriales como aditivos modificadores de la fricción en las superficies desgastadas es el efecto reparador.

Finalmente se ha estudiado el rendimiento tribológico de nanolubricantes formados por el aceite base TMPTO con nanopartículas superparamagnéticas recubiertas con ácido oleico: Fe_3O_4 de dos tamaños 6.3 nm y 10 nm, y una aleación de Nd de 19 nm. Para ello, el grupo NANOMAG sintetizó nanopartículas recubiertas mediante coprecipitación química o descomposición térmica mediante adsorción de ácido oleico en el mismo paso, con el fin de lograr una buena estabilidad de las mismas en el seno del aceite. Se prepararon tres nanodispersiones de TMPTO de 0.015 wt% de cada nanopartícula, las cuales mostraron una sobresaliente estabilidad de al menos once meses. En cuanto a los ensayos tribológicos, se han llevado a cabo dos tipos diferentes de pruebas tribológicas: condiciones de deslizamiento puro y condiciones de rodadura (relación de deslizamiento rodadura del 5%). Tanto la fricción como el desgaste han disminuido para todos los nanolubricantes en comparación con el aceite base. El mejor comportamiento tribológico se encontró para la nanodispersión de nanopartículas de aleación de Nd, con reducciones de 29% y 67% en fricción y ancho de huella de desgaste, respectivamente, en comparación con TMPTO. A través de la espectroscopia Raman y las medidas de rugosidad en las huellas desgastadas se puede concluir que los mecanismos que explican el papel de estas nanopartículas como aditivos de lubricante TMPTO son la formación de tribofilm, que es un efecto directo de la nanopartícula sobre la superficie desgastada, así como los efectos de reparación y pulido. Por otro lado, con las condiciones de rodadura, se realizaron ensayos para determinar la fricción a través de curvas de Stribeck así como el espesor de la película de los nanolubricantes, obteniendo que el nanolubricante Fe_3O_4 (6.3 nm) reduce la fricción en comparación con TMPTO, mientras que el comportamiento de los otros dos nanolubricantes es similar al del aceite base.

Finalmente se realizaron también medidas de par de fricción en una máquina de rodamientos, observando que el nanolubricante de Fe_3O_4 (6.3 nm) presenta un mejor comportamiento que el aceite base TMPTO.

Todas estas investigaciones han llevado a cumplir el objetivo principal de esta Tesis Doctoral ya que se han diseñado y caracterizado nanolubricantes eficientes formados por la adición de nanomateriales en algunos ésteres y aceites base PAO.

USC
UNIVERSIDADE
DE SANTIAGO
DE COMPOSTELA

USC

UNIVERSIDADE DE SANTIAGO DE COMPOSTELA